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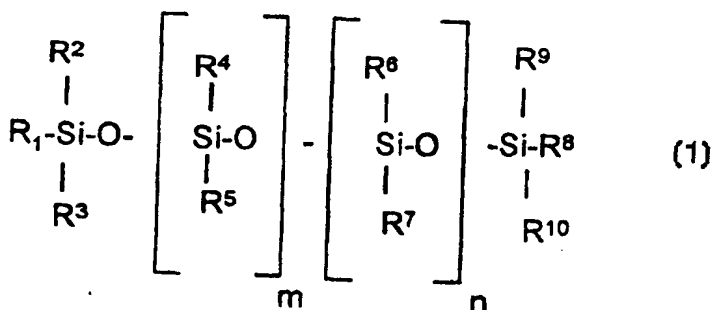
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(54) Title: FABRIC COLOR PROTECTION COMPOSITIONS AND METHODS

(57) Abstract

Provided are methods of washing fabric articles in the presence of silicone oils to provide for color protection and/or fragrance retention in the washing of fabric articles with detergents. Fabric articles are washed in a washing medium comprised of a major amount by weight of water, a first minor amount by weight of a detergent and a second minor amount by weight of an aminosilicone having formula (1). Also provided are powder detergent compositions, without inorganic phosphates, for washing textiles, in particular colored textiles, comprising: at least one surface-active agent, at least one inorganic or organic builder which is soluble in the washing liquor, and at least one aminosilicone.



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FABRIC COLOR PROTECTION COMPOSITIONS AND METHODS

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10 Field of the Invention

The present invention relates to methods of washing fabric articles in the presence of silicone compounds to provide for color protection and/or fragrance retention in the washing of fabric articles with
15 detergents. The present invention also relates to preferred compositions for use in the washing of fabric articles with detergents. Another subject of the present invention is powder detergent compositions, without inorganic phosphates, for washing textiles, in particular colored textiles, said compositions comprising at least one aminosilicone and being
20 capable of forming a washing liquor which is free of or which only contains a small proportion of inorganic substances which are insoluble in said liquor. It is also targeted at a process for protecting textiles, in particular colored textiles, by washing the said textiles using an aqueous liquor containing said compositions.

25

Background Discussion

The use of various agents to soften fabrics is known in the art. For example, EP 585 040 A1 discloses a fabric softening composition comprising at least 1% by weight of a particular quaternary ammonium
30 compound. EP 612 841 A2 discloses the use of a fabric softening clay on keratin containing fibers for controlling and for preventing pilling.

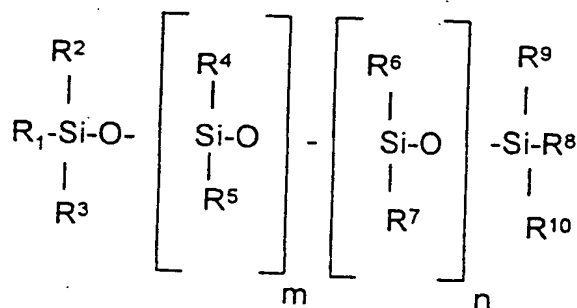
The use of certain silicone oils in detergent compositions to effect fabric softening and certain other benefits is disclosed e.g. in EP 150

872, EP 150 867 and FR 2 713 237. It is known (US-A-4,585,563, WO 92/07927) to use aminosilicones in powder detergent compositions for washing laundry, in order to contribute advantages, such as softness, anti-static behavior, ease of ironing or resistance to creasing, to the
 5 fibers, in particular cotton fibers.

Summary of the Invention

1. General Color Protection Method

In one aspect, this invention relates to a method comprising
 10 washing a colored fabric article in a washing medium comprised of a major amount by weight of water, a first minor amount by weight of a detergent and a second minor amount by weight of an aminosilicone compound having the formula:



wherein:

R¹ and R⁸ are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically C₁-C₄) and alkoxy (typically C₁-C₄),

20 R², R³, R⁹, and R¹⁰ are independently selected from the group consisting of alkyl (typically C₁-C₄) and alkoxy (typically C₁-C₄), provided that one of R², R³, R⁹, and R¹⁰ may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted

aminoalkyl group such that the compound will have both primary and secondary amine functionality),

R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically C_1 - C_4) and aryl (typically phenyl),

5 R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and

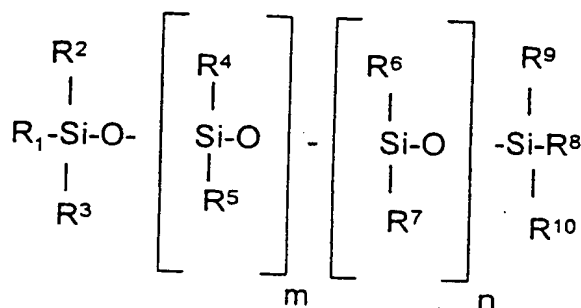
m and n are numbers wherein m is greater than n (typically the
10 ratio of $m:n$ is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of about 10 to about 100,000 cps at 25°C (typically the sum of n and m is from about 5 to about 600, more typically from about 50 to about 400 and
15 most typically from about 135 to about 275),

wherein said first minor amount by weight is greater than said second minor amount by weight. In preferred embodiments of this method, said washing medium is the product of mixing water with a composition comprised of said aminosilicone compound in association
20 with an insoluble support. In particularly preferred embodiments, an aminosilicone compound wherein R^1 and R^8 are both alkoxy, (typically methoxy) is employed. Preferably, the washing is repeated successively with at least about ten successive washing media. It has been found that the use of said washing medium is effective to prevent fading of the color
25 of said fabric after said washings.

2. General Fragrance Retention Method

In another aspect, this invention relates to a method of washing a fabric article in a washing medium comprised of a major amount by
30 weight of water, a first minor amount by weight of a detergent, a second

minor amount by weight of an aminosilicone compound having the formula:



5

wherein:

R^1 and R^8 are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically $\text{C}_1\text{-C}_4$) and alkoxy (typically $\text{C}_1\text{-C}_4$),

R^2 , R^3 , R^9 , and R^{10} are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$) and alkoxy (typically $\text{C}_1\text{-C}_4$), provided that one of R^2 , R^3 , R^9 , and R^{10} may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),

R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$) and aryl (typically phenyl),

R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and

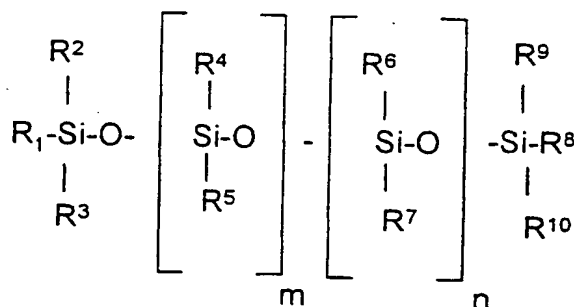
m and n are numbers wherein m is greater than n (typically the ratio of $m:n$ is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity

of about 10 to about 100,000 cps at 25°C (typically the sum of n and m is from about 5 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275),

and a third minor amount by weight of a fragrance, wherein said first minor amount by weight is greater than each of said second minor amount by weight and said third minor amount by weight. In preferred embodiments, said washing medium is the product of mixing water with a composition comprised of said aminosilicone compound in association with an insoluble support. In particularly preferred embodiments, an aminosilicone compound wherein R¹ and R⁸ are both alkoxy is employed. It has been found that the use of said washing medium is effective to prolong the release of said fragrance from said fabric article after said washing.

3. General Detergent Composition with Insoluble Support

This invention also relates to a detergent composition comprising a major amount by weight of a detergent and a first minor amount by weight of an aminosilicone compound having the formula:



wherein:

R¹ and R⁸ are independently alkoxy (typically C₁-C₄),

R², R³, R⁹, and R¹⁰ are independently selected from the group consisting of alkyl (typically C₁-C₄) and alkoxy (typically C₁-C₄), provided that one of R², R³, R⁹, and R¹⁰ may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-

substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),

5 R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically C_1 - C_4) and aryl (typically phenyl),

R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and

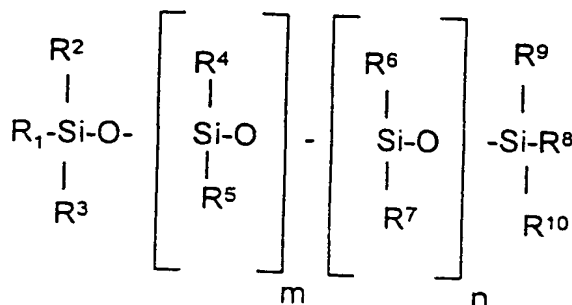
10 m and n are numbers wherein m is greater than n (typically the ratio of $m:n$ is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of about 10 to about 100,000 cps at 25° (typically the sum of n and m is
15 from about 5 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275),

and a second minor amount by weight of an insoluble support, wherein said aminosilicone compound is in association with said insoluble support.

20

4. General Color Protection Method with Insoluble Support

This invention further relates to a method comprising washing a fabric article in a washing medium comprised of a major amount by weight of water and a first minor amount by weight of a detergent, a
25 second minor amount by weight of an aminosilicone compound having the formula:



wherein:

R^1 and R^8 are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically $\text{C}_1\text{-C}_4$) and alkoxy (typically $\text{C}_1\text{-C}_4$)

5 R^2 , R^3 , R^9 , and R^{10} are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$), and alkoxy (typically $\text{C}_1\text{-C}_4$), provided that one of R^2 , R^3 , R^9 , and R^{10} may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),

R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$) and aryl (typically phenyl),

15 R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality), and

m and n are numbers wherein m is greater than n (typically the ratio of $m:n$ is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of about 10 to about 100,000 cps at 25°C (typically the sum of n and m is from about 5 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275),

and a third minor amount by weight of an insoluble support, wherein said aminosilicone compound is in association with said insoluble support, wherein said first minor amount is greater than each of said second minor amount and said third minor amount. In certain preferred embodiments, said fabric article is a colored fabric article. In other preferred embodiments, said detergent composition is further comprised of a fragrance in a minor amount by weight, more typically about 0.05 to about 0.5%, more typically about 0.08 to about 0.12%.

10 5. Soluble Powder Detergent Compositions Without Inorganic Phosphates

Powder detergent compositions, without inorganic phosphates (alkali metal tripolyphosphates), contributing effective protection to textiles, in particular to colored textiles, have now been found.

15 According to a first subject of this invention, it concerns powder detergent compositions, without inorganic phosphates, comprising,

- at least one surface-active agent (S)
- at least one inorganic or organic builder (B) which is soluble in the washing liquor
- 20 - and at least one aminosilicone (AS),

said compositions not comprising more than 20% of their weight of inorganic substances which are insoluble in the washing liquor.

The builder is regarded as "soluble" when it is capable of dissolving to more than 80% of its weight in the washing liquor.

25 An inorganic substance is regarded as "insoluble" when its solubility is less than 20% of its weight in the washing liquor.

Washing liquor is understood to mean the liquor obtained by dilution of the detergent composition during the prewashing and/or washing cycle or cycles.

A second subject of this invention consists of a process for protecting textiles, in particular colored textiles, by washing said textiles using an aqueous liquor containing water and an effective amount of the said compositions containing an aminosilicone as defined above. The said aqueous liquor can contain of the order of 0.5 to 10 grams/litre of detergent composition containing an aminosilicone. It can relate to industrial or domestic washing operations, in a washing machine or by hand. The washing operations can be carried out at a temperature of the order of 25 to 90°C, preferably of 30 to 60°C.

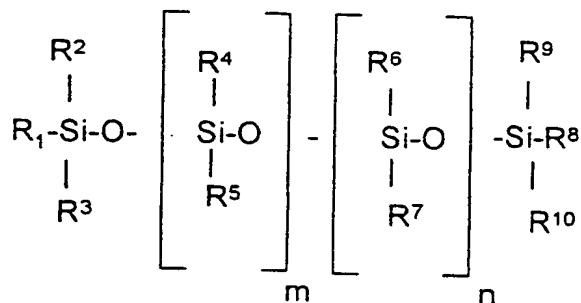
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Detailed Description of the Preferred Embodiments

I. Aminoalkyl/alkoxysilane-silicone Compounds

One of the components of the compositions and methods of this invention is an aminosilicone compound of the formula:

15



wherein:

R¹ and R⁸ are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically C₁-C₄) and alkoxy (typically C₁-C₄),

R², R³, R⁹, and R¹⁰ are independently selected from the group consisting of alkyl (typically C₁-C₄) and alkoxy (typically C₁-C₄), provided that one of R², R³, R⁹, and R¹⁰ may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted

aminoalkyl group such that the compound will have both primary and secondary amine functionality),

R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically C_1 - C_4) and aryl (typically phenyl),

5 R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(aminoalkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),

m and n are numbers wherein m is greater than n (typically the
10 ratio of m:n is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of about 10 to about 100,000 cps at 25° (typically the sum of n and m is from about 5 to about 600, more typically from about 50 to about 400 and
15 most typically from about 135 to about 275).

The preparation and properties of silicone compounds is discussed generally in Silicones: Chemistry and Technology, pp. 21-31 and 75-90 (CRC Press, Vulkan- Verlag, Essen, Germany, 1991) and in Harman et al. "Silicones", Encyclopedia of Polymer Science and
20 Engineering, vol. 15, pp. (John Wiley & Sons, Inc. 1989), the disclosures of which are incorporated herein by reference. Preferred aminosilicone compounds are disclosed, for example in JP-047547 (J57161170) (Shinetsu Chem. Ind. KK). Particularly preferred aminosilicone compounds are the three of formula I wherein (1) R^1 and R^8 are methoxy,
25 R^2 , R^3 , R^4 , R^5 , R^6 , R^9 , and R^{10} are methyl, R^7 is N-aminoethyl-3-aminopropyl, m is about 135, and n is about 1.5, (2) R^1 and R^8 are methoxy, R^2 , R^3 , R^4 , R^5 , R^6 , R^9 , and R^{10} are methyl, R^7 is N-aminoethyl-3-aminopropyl, m is about 270, and n is about 1.5, and (3) R^1 and R^8 are ethoxy, R^2 , R^3 , R^4 , R^5 , R^6 , R^9 , and R^{10} are methyl, R^7 is 3-aminopropyl, m
30 is about 135, and n is about 1.5. Other aminosilicone compounds include

those wherein R¹, R², and R⁶ are ethoxy, R³ is 3-aminopropyl, R⁴, R⁵, R⁶, R⁹, and R¹⁰ are methyl, m is about 8, and n is zero. Of course, for pure aminosilicone compounds, the numbers m and n will be integers, but for mixtures of compounds, m and n will be expressed as fractions or compound numbers which represent an average of the compounds present. Further, the formula above is not meant to imply a block copolymer structure, thus, the aminosilicone compound may have a random or block structure. Typically, at least about 50% by weight of the R⁴, R⁵, and R⁶ groups will be methyl groups, more typically at least about 90% and even more typically about 100%.

The aminosilicone compound typically will be in the form of a liquid or viscous oil at room temperature.

The aminosilicones described below in the context of the soluble powder detergent compositions can be substituted for the aminosilicones described above.

II. Insoluble Carriers

While the aminosilicone can be used in certain compositions and methods of this invention alone or as an aqueous emulsion, the aminosilicone is preferably used in association with a water-insoluble solid carrier, for example, clays, natural or synthetic silicates, silica, resins, waxes, starches, ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite, bentonite or diatomaceous earth, or ground synthetic minerals, such as silica, alumina, or silicates especially aluminum or magnesium silicates. Useful inorganic agents comprise those of natural or synthetic mineral origin. Specific examples of carriers include diatomaceous earths, e.g. Celite Registered TM (Johns Manville Corp., Denver, Col.) and the smectite clays such as the saponites and the montmorillonite colloidal clays such as Veegum Registered TM and Van Gel Registered TM (Vanderbilt

Minerals, Murray, KY), or Magnabrite Registered TM (American Colloid Co., Skokie, IL). Synthetic silicate carriers include the hydrous calcium silicate, Micro-Cel Registered TM and the hydrous magnesium silicate Celkate Registered TM (Seegot, Inc., Parsippany, NJ). Inosilicates carriers such as the naturally-occurring calcium meta-silicates such as wollastonite, available as the NYAD Registered TM wollastonite series (Processed Minerals Inc., Willsboro, NY) can also be mentioned. Synthetic sodium magnesium silicate clays, hectorite clays, and fumed silicas can also be mentioned as carriers. The carrier can be a very finely divided material of average particle diameter below 0.1 micron. Examples of such carriers are fumed silica and precipitated silica; these generally have a specific surface (BET) of above 40 m² /g.

The clays that are particularly useful elements of the compositions and methods of this invention are those which cooperate with the silicone compounds to wash laundry better than would be expected from the actions of the individual components in detergent compositions. Such clays include the montmorillonite-containing clays which have swelling properties (in water) and which are of smectite structure. Typical of the smectite clays for use in the present invention is bentonite and typically the best of the bentonites are those which have a substantial swelling capability in water, such as the sodium bentonites, the potassium bentonites, or which are swellable in the presence of sodium or potassium ions, such as calcium bentonite. Such swelling bentonites are also known as western or Wyoming bentonites, which are essentially sodium bentonite. Other bentonites, such as calcium bentonite, are normally non-swelling. Among the preferred bentonites are those of sodium and potassium, which are normally swelling, and calcium and magnesium, which are normally non-swelling, but are swellable. Of these it is preferred to utilize calcium (with a source of sodium being present) and sodium bentonites. The bentonites employed are not limited to those

produced in the United States of America, such as Wyoming bentonite, but also may be obtained from Europe, including Italy and Spain, as calcium bentonite, which may be converted to sodium bentonite by treatment with sodium carbonate, or may be employed as calcium
5 bentonite. Typically, the clay will have a high montmorillonite content and a low content of cristobalite and/or quartz. Also, other montmorillonite-containing smectite clays of properties like those of the bentonites described may be substituted in whole or in part for the bentonites described herein, but typically the clay will be a sodium
10 bentonite with high montmorillonite content and low cristobalite and quartz contents.

The swellable bentonites and similarly operative clays are of ultimate particle sizes in the micron range, e.g., 0.01 to 20 microns and of actual particle sizes less than 100 or 150 microns, such as 40 to 150
15 microns or 45 to 105 microns. Such size ranges also apply to the zeolite builders, which will be described later herein. The bentonite and other such suitable swellable clays may be agglomerated to larger particle sizes too, such as up to 2 or 3 mm. in diameter.

The ratio of aminosilicone compound to carrier will typically range
20 from about 0.001 to about 2, more typically from about 0.02 to about 0.5, and most typically from about 0.1 to about 0.3.

III. Detergents

The methods and compositions of this invention all employ a
25 detergent, and optionally, other functional ingredients. Examples of the detergents and other functional ingredients that can be used are disclosed in U.S. Serial No. 08/726,437, filed October 4, 1996, the disclosure of which is incorporated herein by reference. The detergent can be selected from a wide variety of surface active agents.

A. Nonionic Surfactants

Nonionic surfactants, including those having an HLB of from 5 to 17, are well known in the detergency art. Examples of such surfactants are listed in U.S. Patent No. 3,717,630, Booth, issued February 20, 1973, and U. S. Patent No. 3,332,880, Kessler et al., issued July 25, 1967, each of which is incorporated herein by reference. Nonlimiting examples of suitable nonionic surfactants which may be used in the present invention are as follows:

- (1) The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, said ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene, and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol; and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630, marketed by Rhone-Poulenc Inc. and Triton X-45, X-114, X-100, and X-102, all marketed by Union Carbide.
- (2) The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of

myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol; and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants in this type include Tergitol 15-S-9, marketed by Union Carbide Corporation, Neodol 45-9, Neodol 23-6.5, Neodol 45-7, and Neodol 45-4, marketed by Shell Chemical Company.

- (3) The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds typically has a molecular weight of from about 1500 to 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available Pluronic surfactants, marketed by Wyandotte Chemical Corporation.
- (4) The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, said moiety having a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include

certain of the commercially available Tetronic compounds, marketed by Wyandotte Chemical Corporation.

- (5) Semi-polar nonionic detergent surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbons atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred semi-polar nonionic detergent surfactants are the amine oxide detergent surfactants having the formula

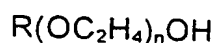


wherein R^1 is an alkyl, hydroxy alkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms. R^2 is an alkylene or hydroxy alkylene group containing from 2 to 3 carbon atoms or mixtures thereof, x is from 0 to about 3 and each R^3 is an alkyl or hydroxy alkyl group containing from 1 to about 3 carbon atoms or a polyethylene oxide group containing from one to about 3 ethylene oxide groups and said R^3 groups can be attached to each other, e.g., through an oxygen or nitrogen atom to form a ring structure.

Preferred amine oxide detergent surfactants are C_{10} - C_{18} alkyl dimethyl amine oxide, C_8 - C_{18} alkyl dihydroxy ethyl amine oxide, and C_{8-12} alkoxy ethyl dihydroxy ethyl amine oxide.

Nonionic detergent surfactants (1)-(4) are conventional ethoxylated nonionic detergent surfactants and mixtures thereof can be used.

Preferred alcohol ethoxylate nonionic surfactants for use in the compositions of the liquid, powder, and gel applications are biodegradable and have the formula



wherein R is a primary or secondary alkyl chain of from about 8 to about 22, preferably from about 10 to about 20 carbon atoms and n is an average of from about 2 to about 12, particularly from about 2 to about 9. The nonionics have an HLB (hydrophilic-lipophilic balance) of from about 5 to about 17, preferably from about 6 to about 15. HLB is defined in detail in Nonionic Surfactants, by M. J. Schick, Marcel Dekker, Inc., 1966, pages 606-613, incorporated herein by reference. In preferred nonionic surfactants, n is from 3 to 7. Primary linear alcohol ethoxylates (e.g., alcohol ethoxylates produced from organic alcohols which contain about 20% 2-methyl branched isomers, commercially available from Shell Chemical Company under the trademark Neodol) are preferred from a performance standpoint.

Particularly preferred nonionic surfactants for use in liquid, powder, and gel applications include the condensation product of C₁₀ alcohol with 3 moles of ethylene oxide; the condensation product of tallow alcohol with 9 moles of ethylene oxide; the condensation product of coconut alcohol with 5 moles of ethylene oxide; the condensation product of coconut alcohol with 6 moles of ethylene oxide; the condensation product of C₁₂ alcohol with 5 moles of ethylene oxide; the condensation product of C₁₂₋₁₃ alcohol with 6.5 moles of ethylene oxide, and the same condensation product which is stripped so as to remove substantially all lower ethoxylate and nonethoxylated fractions; the condensation product of C₁₂₋₁₃ alcohol with 2.3 moles of ethylene oxide, and the same

condensation product which is stripped so as to remove substantially all lower ethoxylated and nonethoxylated fractions; the condensation product of C₁₂₋₁₃ alcohol with 9 moles of ethylene oxide; the condensation product of C₁₄₋₁₅ alcohol with 2.25 moles of ethylene oxide; the
5 condensation product of C₁₄₋₁₅ alcohol with 4 moles of ethylene oxide; the condensation product of C₁₄₋₁₅ alcohol with 7 moles of ethylene oxide; and the condensation product of C₁₄₋₁₅ alcohol with 9 moles of ethylene oxide. For bar soap applications, nonionic surfactants are preferably solids at room temperature with a melting point above about 25° C., preferably
10 above about 30° C. Bar compositions of the present invention made with lower melting nonionic surfactants are generally too soft, not meeting the bar firmness requirements of the present invention.

Also, as the level of nonionic surfactant increases, i.e., above about 20% by weight of the surfactant, the bar can generally become oily.

15 Examples of nonionic surfactants usable herein, but not limited to bar applications, include fatty acid glycerine and polyglycerine esters, sorbitan sucrose fatty acid esters, polyoxyethylene alkyl and alkyl allyl ethers, polyoxyethylene lanolin alcohol, glycerine and polyoxyethylene glycerine fatty acid esters, polyoxyethylene propylene glycol and sorbitol
20 fatty acid esters, polyoxyethylene lanolin, castor oil or hardened castor oil derivatives, polyoxyethylene fatty acid amides, polyoxyethylene alkyl amines, alkylpyrrolidone, glucamides, alkylpolyglucosides, and mono- and dialkanol amides.

Typical fatty acid glycerine and polyglycerine esters, as well as
25 typical sorbitan sucrose fatty acid esters, fatty acid amides, and polyethylene oxide/polypropylene oxide block copolymers are disclosed by U.S. Patent No. 5,510,042, Hartman et al, incorporated herein by reference.

The castor oil derivatives are typically ethoxylated castor oil. It is
30 noted that other ethoxylated natural fats, oils or waxes are also suitable.

Polyoxyethylene fatty acid amides are made by ethoxylation of fatty acid amides with one or two moles of ethylene oxide or by condensing mono-or diethanol amines with fatty acid.

Polyoxyethylene alkyl amines include those of formula: RNH-
5 (CH₂CH₂O)_n-H, wherein R is C₆ to C₂₂ alkyl and n is from 1 to about 100.

Monoalkanol amides include those of formula: RCONHR'¹OH, wherein R is C₆-C₂₂ alkyl and R'¹ is C₁ to C₆ alkylene. Dialkanol amides are typically mixtures of:

diethanolamide: RCON(CH₂CH₂OH)₂;
10 amide ester: RCON(CH₂CH₂OH)-CH₂CH₂OOCH₂CH₂OH;
amine ester: RCOOCH₂CH₂NHCH₂CH₂OH; and
amine soap: RCOOH₂N(CH₂CH₂OH)₂,

wherein R in the above formulas is an alkyl of from 6 to 22 carbon atoms.

Examples of preferred but not limiting surfactants for detergent bar
15 products are the following:

Straight-Chain Primary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, and pentadeca-ethoxylates of n-hexadecanol, and n-hexadecanol, and n-octadecanol
20 having an HLB within the range recited herein are useful nonionics in the context of this invention. Exemplary ethoxylated primary alcohols useful herein as the conventional nonionic surfactants of the compositions are n-C₁₈EO(10); n-C₁₄EO(13); and n-C₁₀EO(11). The ethoxylates of mixed natural or synthetic alcohols in the "tallow" chain length range are also
25 useful herein. Specific examples of such materials include tallow-alcohol-EO(11), tallow-alcohol-EO(18), and tallow-alcohol-EO(25).

Straight-Chain Secondary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-,
30 and nonadeca-ethoxylates of 3-hexadecanol, 2-octadecanol, 4-

eicosanol, and 5-eicosanol having an HLB within the range recited herein are useful conventional nonionics in the context of this invention. Exemplary ethoxylated secondary alcohols useful herein are 2-C₁₆EO(11); 2-C₂₀EO(11); and 2-C₁₆EO(14).

5

Alkyl Phenol Alkoxylates

As in the case of the alcohol alkoxylates, the hexa- through octadeca-ethoxylates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the range recited herein are useful as
10 conventional nonionic surfactants in the instant compositions. The hexa-through octadeca-ethoxylates of p-tridecylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful in the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18). Especially preferred is Nonyl Nonoxynol-49
15 known as Igepal[®] DM-880 from Rhone-Poulenc Inc.

As used herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an
20 equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

Olefinic Alkoxylates

25 The alkenyl alcohols, both primary and secondary, and alkenyl phenols corresponding to those disclosed immediately hereinabove can be ethoxylated to an HLB within the range recited herein and used as the conventional nonionic surfactants of the instant compositions.

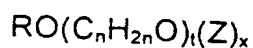
Branched Chain Alkoxylates

Branched chain primary and secondary alcohols which are available can be ethoxylated and employed as conventional nonionic surfactants in compositions herein.

5 The above ethoxylated nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

Alkylpolysaccharides

10 Still further suitable nonionic surfactants of this invention include alkylpolysaccharides, preferably alkylpolyglycosides of the formula:



wherein

Z is derived from glyucose;

15 R is a hydrophobic group selected from the group consisting of a C₁₀-C₁₈, preferably a C₁₂-C₁₄, alkyl group, alkyl phenyl group, hydroxyalkyl group, hydroxyalkylphenyl group, and mixtures thereof;

n is 2 or 3; preferably 2;

t is from 0 to 10; preferably 0; and

20 x is from 1.5 to 8; preferably 1.5 to 4; more preferably from 1.6 to 2.7.

These surfactants are disclosed in U.S. Patent Nos. 4,565,647, Llenado, issued January 21, 1986; 4,536,318, Cook et al., issued August 20, 1985; 4,536,317, Llenado et al., issued August 20, 1985; 4,599,188 Llenado, issued July 8, 1986; and 4,536,319, Payne, issued August 20, 1985; all of which are incorporated herein by reference.

25 The compositions of the present invention can also comprise mixtures of the above nonionic surfactants.

A thorough discussion of nonionic surfactants for detergent bar and liquid products is presented by U.S. Patent Nos. 5,510,042, Hartman et al., and 4,483,779, Llenado, et al., incorporated herein by reference.

5 B. Anionic Surfactants

Anionic surfactants include any of the known hydrophobes attached to a carboxylate, sulfonate, sulfate or phosphate polar, solubilizing group including salts. Salts may be the sodium, potassium, ammonium and amine salts of such surfactants. Useful anionic
10 surfactants can be organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester group, or mixtures thereof. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic deterative surfactants which can be
15 used in the present invention are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms) produced from the glycerides of tallow or coconut oil; and alkyl benzene sulfonates.

Other useful anionic surfactants herein include the esters of alpha-sulfonated fatty acids preferably containing from about 6 to 20 carbon
20 atoms in the ester group; 2-acyloxyalkane-1-sulfonic acids preferably containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates preferably containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; olefin
25 sulfonates preferably containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates preferably containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactants based on the higher fatty acids, i.e., "soaps"
30 are useful anionic surfactants herein. Higher fatty acids containing from

about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms and the coconut and tallow soaps can also be used herein as corrosion inhibitors.

Preferred water-soluble anionic organic surfactants herein include
5 linear alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; branched alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl sulfonates; alkyl ether (ethoxylated) sulfates wherein the alkyl moiety contains from
10 about 12 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 and 12, especially 3 to 9; the sulfated condensation products of tallow alcohol with from about 3 to 12, especially 6 to 9, moles of ethylene oxide; and olefin sulfonates containing from about 14 to 16 carbon atoms.

15 Specific preferred anionics for use herein include: the linear C₁₀-C₁₄ alkyl benzene sulfonates (LAS); the branched C₁₀-C₁₄ alkyl benzene sulfonates (ABS); the tallow alkyl sulfates, the coconut alkyl glyceryl ether sulfonates; the sulfated condensation products of mixed C₁₀-C₁₈ tallow alcohols with from about 1 to about 14 moles of ethylene oxide; and the
20 mixtures of higher fatty acids containing from 10 to 18 carbon atoms.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures. Moreover, commercial grades of the surfactants can contain non-interfering components which are processing by-products. For example, commercial alkaryl sulfonates,
25 preferably C₁₀-C₁₄, can comprise alkyl benzene sulfonates, alkyl toluene sulfonates, alkyl naphthalene sulfonates and alkyl poly-benzenoid sulfonates. Such materials and mixtures thereof are fully contemplated for use herein.

Other examples of the anionic surfactants used herein include fatty
30 acid soaps, ether carboxylic acids and salts thereof, alkane sulfonate

salts, *a*-olefin sulfonate salts, sulfonate salts of higher fatty acid esters, higher alcohol sulfate ester or ether ester salts, alkyl, preferably higher alcohol phosphate ester and ether ester salts, and condensates of higher fatty acids and amino acids.

- 5 Fatty acid soaps include those having the formula: $R-C(O)OM$, wherein R is C_6 to C_{22} alkyl and M is preferably sodium.

Salts of ether carboxylic acids and salts thereof include those having the formula: $R-(OR^1)_n-OCH_2C(O)OM$, wherein R is C_6 to C_{22} alkyl, R^1 is C_2 to C_{10} , preferably C_2 alkyl, and M is preferably sodium.

- 10 Alkane sulfonate salts and *a*-olefin sulfonate salts have the formula: $R-SO_3M$, wherein R is C_6 to C_{22} alkyl or *a*-olefin, respectively, and M is preferably sodium.

Sulfonate salts of higher fatty acid esters include those having the formula:



wherein R is C_{12} to C_{22} alkyl, R^1 is C_1 to C_{18} alkyl and M is preferably sodium.

- Higher alcohol sulfate ester salts include those having the formula:
- 20 $RC(O)O-R^1-OSO_3M,$

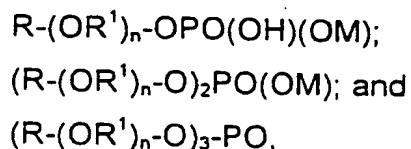
wherein R is C_{12} - C_{22} alkyl, R^1 is C_1 - C_{18} hydroxyalkyl, M is preferably sodium.

Higher alcohol sulfate ether ester salts include those having the formula:



wherein R is C_{12} - C_{22} alkyl, R^1 is C_1 - C_{18} hydroxyalkyl, M is preferably sodium and x is an integer from 5 to 25.

Higher alcohol phosphate ester and ether ester salts include compounds of the formulas:



wherein R is alkyl or hydroxyalkyl of 12 to 22 carbon atoms, R¹ is C₂H₅, n is an integer from 5 to 25, and M is preferably sodium.

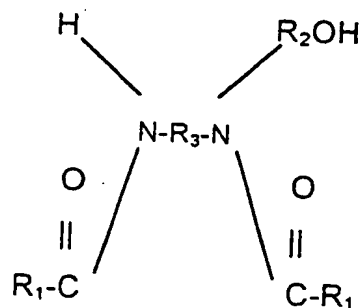
Other anionic surfactants herein are sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

15 C. Cationic Surfactants

Preferred cationic surfactants of the present invention are the reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof.

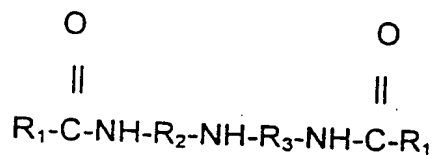
20 A preferred component is a nitrogenous compound selected from the group consisting of:

- (i) the reaction product mixtures of higher fatty acids with hydroxyalkylalkylenediamines in a molecular ratio of about 2:1, said reaction product containing a composition having a compound of the formula:



wherein R_1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group and R_2 and R_3 are divalent C_1 - C_3 alkylene groups; commercially available as Mazamide 6 from PPG;

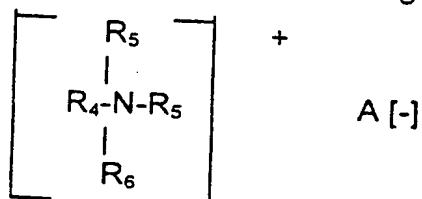
- (ii) the reaction product of higher fatty acids with dialkylenetriamines in a molecular ratio of about 2:1; said reaction product containing a composition having a compound of the formula:



wherein R_1 , R_2 and R_3 are as defined above; and mixtures thereof.

Another preferred component is a cationic nitrogenous salt containing one long chain acyclic aliphatic C_{15} - C_{22} hydrocarbon group selected from the group consisting of:

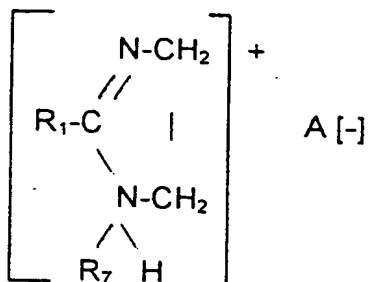
- (i) acyclic quaternary ammonium salts having the formula:



wherein R_4 is an acyclic aliphatic C_{15} - C_{22} hydrocarbon group, R_5 and R_6 are C_1 - C_4 saturated alkyl or hydroxyalkyl groups, and A^- is an anion, especially as described in more detail hereinafter, examples of these surfactants are sold by Sherex Chemical

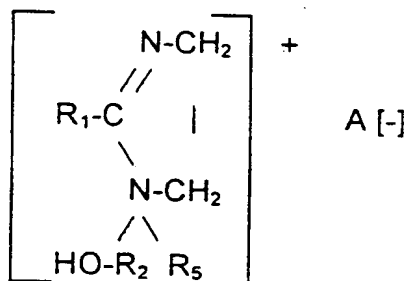
Company under the Adgen trademarks;

- (ii) substituted imidazolinium salts having the formula:



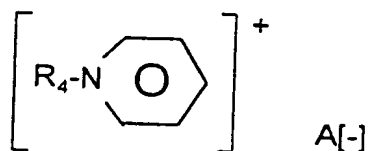
wherein R_1 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{21}$ hydrocarbon group, R_7 is a hydrogen or a $\text{C}_1\text{-C}_4$ saturated alkyl or hydroxyalkyl group, and A^- is an anion;

- (iii) substituted imidazolinium salts having the formula:



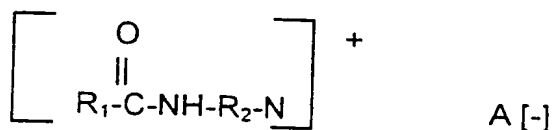
wherein R_2 is a divalent $\text{C}_1\text{-C}_3$ alkylene group and R_1 , R_5 and A^- are as defined above; an example of which is commercially available under the Monaquat ISIES trademark from Mona Industries, Inc.;

- (iv) alkylpyridinium salts having the formula:



wherein R_4 is an acyclic aliphatic $\text{C}_{16}\text{-C}_{22}$ hydrocarbon group and $\text{A} [-]$ is an anion; and

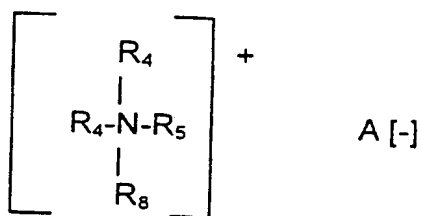
- (v) alkanamide alkylene pyridinium salts having the formula:



wherein R_1 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{21}$ hydrocarbon group, R_2 is a divalent $\text{C}_1\text{-C}_3$ alkylene group, and $\text{A} [-]$ is an ion group; and mixtures thereof.

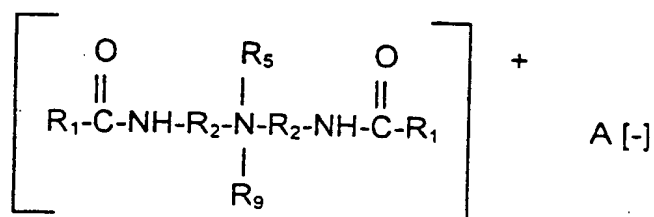
Another class of preferred cationic nitrogenous salts having two or more long chain acyclic aliphatic $\text{C}_{15}\text{-C}_{22}$ hydrocarbon groups or one said group and an arylalkyl group are selected from the group consisting of:

- (i) acyclic quaternary ammonium salts having the formula:



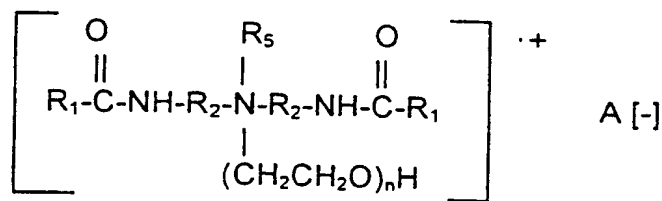
wherein each R_4 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{22}$ hydrocarbon group, R_5 is a $\text{C}_1\text{-C}_4$ saturated alkyl or hydroxyalkyl group, R_8 is selected from the group consisting of R_4 and R_5 groups, and $\text{A} [-]$ is an anion defined as above; examples of which are commercially available from Sherex Company under the Adgen trademarks;

- (ii) diamido quaternary ammonium salts having the formula:



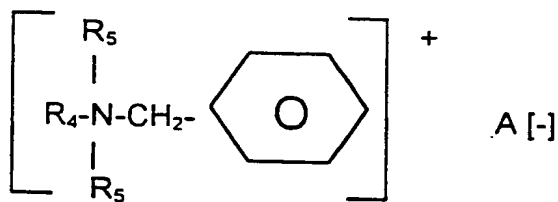
wherein each R_1 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{21}$ hydrocarbon group, R_2 is a divalent alkylene group having 1 to 3 carbon atoms, R_5 and R_9 are $\text{C}_1\text{-C}_4$ saturated alkyl or hydroxyalkyl groups, and A^- is an anion; examples of which are sold by Sherex Chemical Company under the Varisoft trademark;

- (iii) diamino alkoxyated quaternary ammonium salts having the formula:



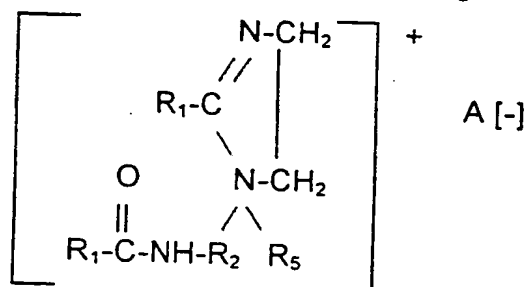
wherein n is equal to 1 to about 5, and R_1 , R_2 , R_5 and A^- are as defined above;

- (iv) quaternary ammonium compounds having the formula:



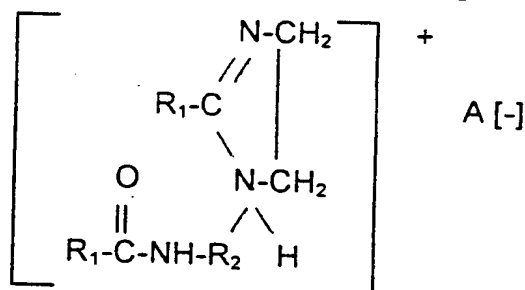
wherein each R_4 is an acyclic aliphatic C_{15} - C_{22} hydrocarbon group, each R_5 is a C_1 - C_4 saturated alkyl or hydroxyalkyl group, and $A [-]$ is an anion; examples of such surfactants are available from Onyx Chemical Company under the Ammonyx[®] 490 trademark;

- (v) substituted imidazolinium salts having the formula:



wherein each R_1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group, R_2 is a divalent alkylene group having 1 to 3 carbon atoms, and R_5 and $A [-]$ are as defined above; examples are commercially available from Sherex Chemical Company under the Varisoft 475 and Varisoft 445 trademarks; and

- (vi) substituted imidazolinium salts having the formula:



wherein R_1 , R_2 and $A -$ are as defined above; and mixtures thereof.

The more preferred cationic conventional surfactant is selected from the group consisting of an alkyltrimethylammonium salt, a dialkyldimethylammonium salt, an alkyldimethylbenzylammonium salt, an

alkylpyridinium salt, an alkylisoquinolinium salt, benzethonium chloride, and an acylamino acid cationic surfactant.

Anion A

5 In the cationic nitrogenous salts herein, the anion A [-] provides electrical neutrality. Most often, the anion used to provide electrical neutrality in these salts is a halide, such as chloride, bromide, or iodide. However, other anions can be used, such as methylsulfate, ethylsulfate, acetate, formate, sulfate, carbonate, and the like. Chloride and
10 methylsulfate are preferred herein as anion A.

Cationic surfactants are commonly employed as fabric softeners in compositions added during the rinse cycle of clothes washing. Many different types of fabric conditioning agents have been used in rinse cycle added fabric conditioning compositions as disclosed by U.S. Patent No.
15 5,236,615, Trinh et al. and U.S. Patent No. 5,405,542, Trinh et al., both patents herein incorporated by reference in their entirety. The most favored type of agent has been the quaternary ammonium compounds. Many such quaternary ammonium compounds are disclosed for example, by U.S. Patent No. 5,510,042, Hartman et al. incorporated herein by
20 reference in its entirety. These compounds may take the form of noncyclic quaternary ammonium salts having preferably two long chain alkyl groups attached to the nitrogen atoms. Additionally, imidazolinium salts have been used by themselves or in combination with other agents in the treatment of fabrics as disclosed by U.S. Patent No. 4,127,489, Pracht, et al., incorporated herein by reference in its entirety. U.S. Patent
25 No. 2,874,074, Johnson discloses using imidazolinium salts to condition fabrics; and U.S. Patent No. 3,681,241, Rudy, and U.S. Patent No. 3,033,704, Sherrill et al. disclose fabric conditioning compositions containing mixtures of imidazolinium salts and other fabric conditioning

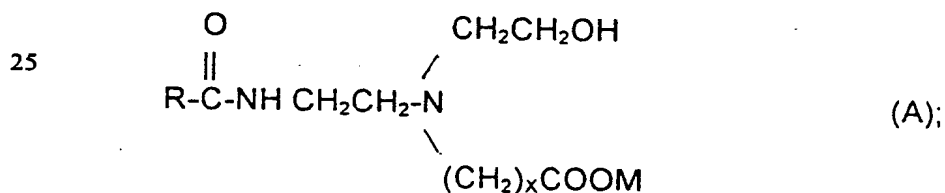
agents. These patents are incorporated herein by reference in their entirety.

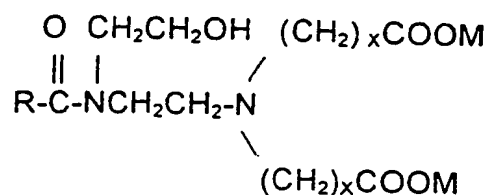
D. Amphoteric Surfactants

5 Amphoteric surfactants have a positive or negative charge or both on the hydrophilic part of the molecule in acidic or alkaline media.

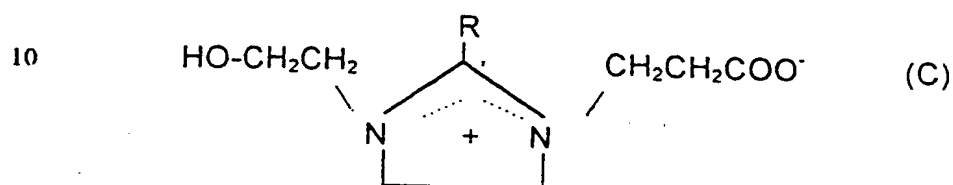
Examples of the amphoteric surfactants which can be used herein include amino acid, betaine, sultaine, phosphobetaines, imidazolinium derivatives, soybean phospholipids, and yolk lecithin. Examples of
10 suitable amphoteric surfactants include the alkali metal, alkaline earth metal, ammonium or substituted ammonium salts of alkyl amphocarboxy glycines and alkyl amphocarboxypropionates, alkyl
amphodipropionates, alkyl amphodiacetates, alkyl amphoglycines and alkyl amphopropionates wherein alkyl represents an alkyl group having 6
15 to 20 carbon atoms. Other suitable amphoteric surfactants include alkyliminopropionates, alkyl iminodipropionates and alkyl
amphopropylsulfonates having between 12 and 18 carbon atoms, alkylbetaines and amidopropylbetaines and alkylsultaines and
alkylamidopropylhydroxy sultaines wherein alkyl represents an alkyl
20 group having 6 to 20 carbon atoms are especially preferred.

Particularly useful amphoteric surfactants include both mono and dicarboxylates such as those of the formulae:





(B); and

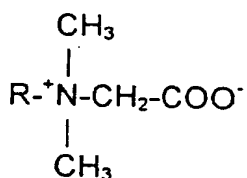


(C)

wherein R is an alkyl group of 6-20 carbon atoms, x is 1 or 2 and M is hydrogen or sodium. Mixtures of the above structures are particularly preferred.

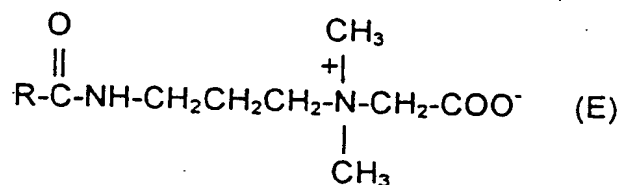
Other formulae for the above amphoteric surfactants include the following:

Alkyl betaines

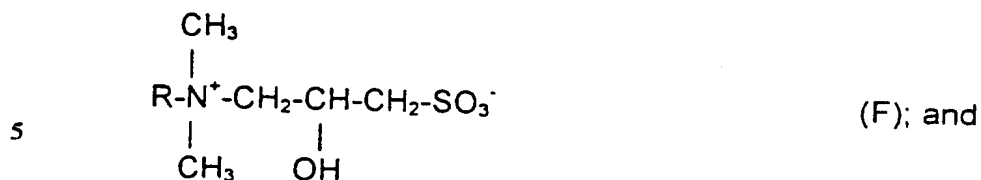


(D);

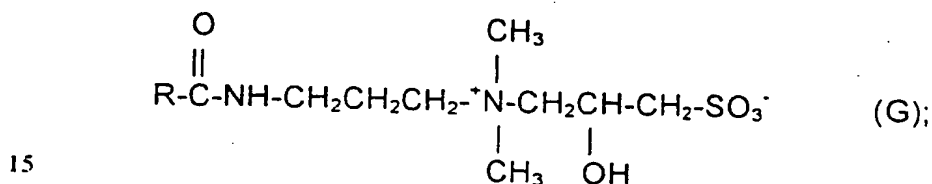
Amidopropyl betaines



(E)

Alkyl sultaines

10 *Alkyl amidopropylhydroxy sultaines*



15 where R is an alkyl group of 6-20 carbon atoms and M is hydrogen or sodium.

Of the above amphoteric surfactants, particularly preferred are the
 20 alkali salts of alkyl amphocarboxyglycinates and alkyl
 amphocarboxypropionates, alkyl amphodipropionates, alkyl
 amphodiacetates, alkyl amphoglycinates, alkyl amphopropyl sulfonates
 and alkyl amphopropionates wherein alkyl represents an alkyl group
 having 6 to 20 carbon atoms. Even more preferred are compounds
 25 wherein the alkyl group is derived from coconut oil or is a lauryl group, for
 example, cocoamphodipropionate. Such cocoamphodipropionate
 surfactants are commercially sold under the trademarks Miranol C2M-SF
 CONC. and Miranol FBS by Rhone-Poulenc Inc.

Other commercially useful amphoteric surfactants are available
 30 from Rhone-Poulenc Inc. and include:

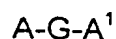
cocoamphoacetate (sold under the trademarks MIRANOL CM CONC. and MIRAPON FA),
cocoamphopropionate (sold under the trademarks MIRANOL CM-SF CONC. and MIRAPON FAS),
cocoamphodiacetate (sold under the trademarks MIRANOL C2M CONC. and MIRAPON FB),
lauroamphoacetate (sold under the trademarks MIRANOL HM CONC. and MIRAPON LA),
lauroamphodiacetate (sold under the trademarks MIRANOL H2M CONC. and MIRAPON LB),
lauroamphodipropionate (sold under the trademarks MIRANOL H2M SF CONC. AND MIRAPON LBS),
lauroamphodiacetate obtained from a mixture of lauric and myristic acids (sold under the trademark MIRANOL BM CONC.), and
cocoamphopropyl sulfonate (sold under the trademark MIRANOL CS CONC.)

Somewhat less preferred are:

caproamphodiacetate (sold under the trademark MIRANOL S2M CONC.),
caproamphoacetate (sold under the trademark MIRANOL SM CONC.),
caproamphodipropionate (sold under the trademark MIRANOL S2M-SF CONC.), and
stearoamphoacetate (sold under the trademark MIRANOL DM).

5 E. Gemini Surfactants

Gemini surfactants form a special class of surfactant. These surfactants have the general formula:



and get their name because they comprise two surfactant moieties (A, A^1)
 10 joined by a spacer (G), wherein each surfactant moiety (A, A^1) has a hydrophilic group and a hydrophobic group. Generally, the two surfactant moieties (A, A^1) are twins, but they can be different.

The gemini surfactants are advantageous because they have low critical micelle concentrations (cmc) and, thus, lower the cmc of solutions containing both a gemini surfactant and a conventional surfactant. Lower cmc causes better solubilization and increased detergency at lower surfactant use levels and unexpectedly enhances the deposition of the soil release polymers as claimed by this invention with demonstrated results to follow herein. Soil removal agents adhere to the fabric being laundered, much better than when mixed with only non-gemini, conventional surfactants.

Also, the gemini surfactants result in a low pC_{20} value and low Krafft points. The pC_{20} value is a measure of the surfactant concentration in the solution phase that will reduce the surface tension of the solvent by 20 dynes/cm. It is a measure of the tendency of the surfactant to adsorb at the surface of the solution. The Krafft point is the temperature at which the surfactant's solubility equals the cmc. Low Krafft points imply better solubility in water, and lead to greater latitude in making formulations.

A number of the gemini surfactants are reported in the literature, see for example, Okahara et al., J. Japan Oil Chem. Soc. 746 (Yukagaku) (1989); Zhu et al., 67 JAOCS 7,459 (July 1990); Zhu et al., 68 JAOCS 7,539 (1991); Menger et al., J. Am. Chemical Soc. 113, 1451 (1991); Masuyama et al., 41 J. Japan Chem. Soc. 4,301 (1992); Zhu et al., 69 JAOCS 1,30 (Jan. 1992); Zhu et al., 69 JAOCS 7,626 July 1992); Menger et al., 115 J. Am. Chem. Soc. 2, 10083 (1993); Rosen, Chemtech 30 (March 1993); and Gao et al., 71 JAOCS 7,771 (July 1994), all of this literature incorporated herein by reference.

Also, gemini surfactants are disclosed by U.S. Patent Nos. 2,374,354, Kaplan; 2,524,218, Bersworth; 2,530,147 Bersworth (two hydrophobic tails and three hydrophilic heads); 3,244,724, Guttman; 5,160,450, Okahara, et al., all of which are incorporated herein by reference.

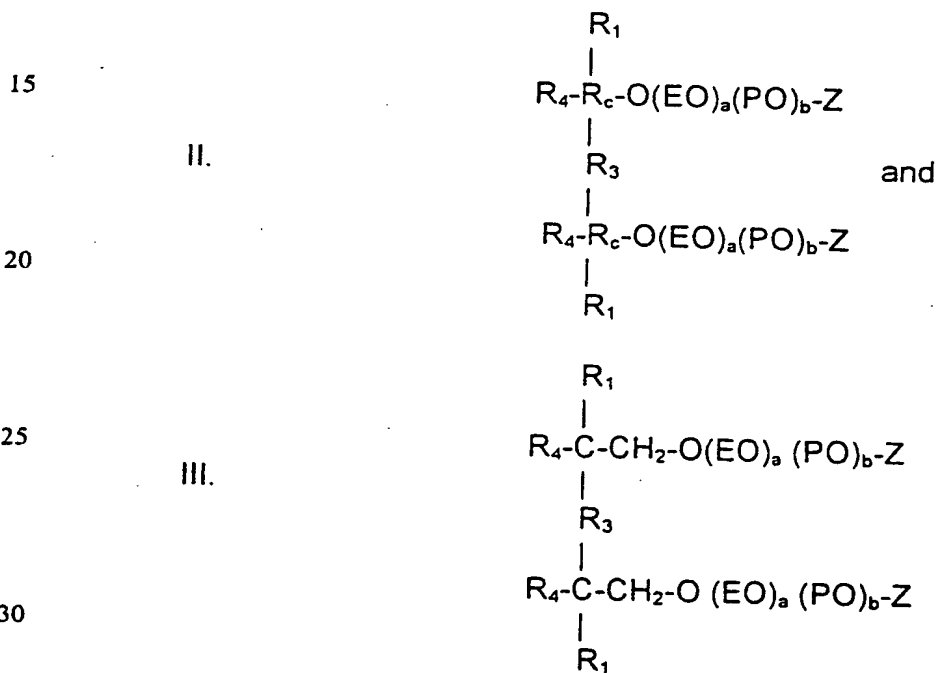
The gemini surfactants may be anionic, nonionic, cationic or amphoteric. The hydrophilic and hydrophobic groups of each surfactant moiety (A,A') may be any of those known to be used in conventional surfactants having one hydrophilic group and one hydrophobic group.

5 For example, a typical nonionic gemini surfactant, e.g., a bis-polyoxyethylene alkyl ether, would contain two polyoxyethylene alkyl ether moieties.

Each moiety would contain a hydrophilic group, e.g., polyethylene oxide, and a hydrophobic group, e.g., an alkyl chain.

10

Gemini surfactants specifically useful in the present invention include gemini anionic or nonionic surfactants of the formulae:



wherein R_c represents aryl, preferably phenyl.

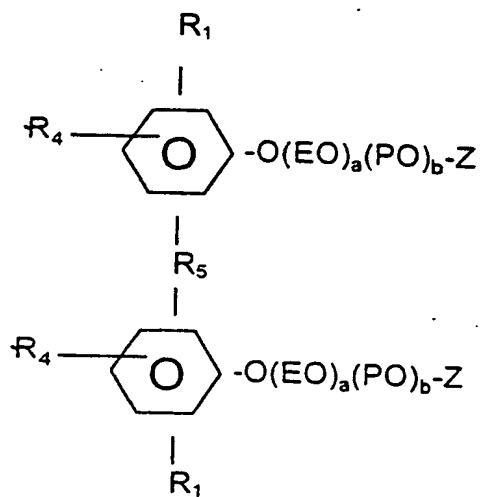
R_1 , R_3 , R_4 , Y , Z , a and b are as defined above.

35

More specifically, these compounds comprise:

5

IV.

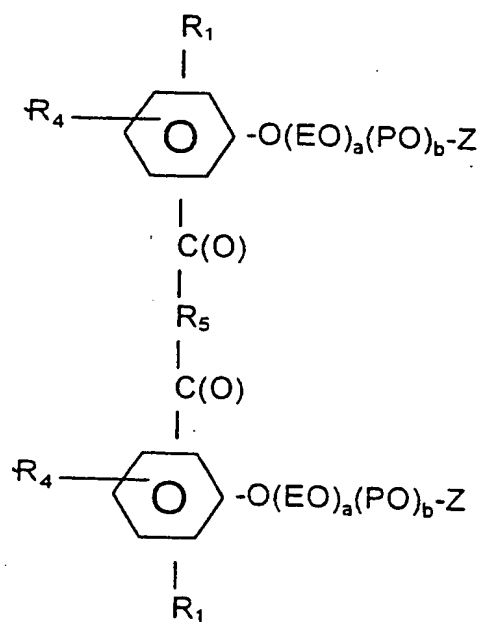


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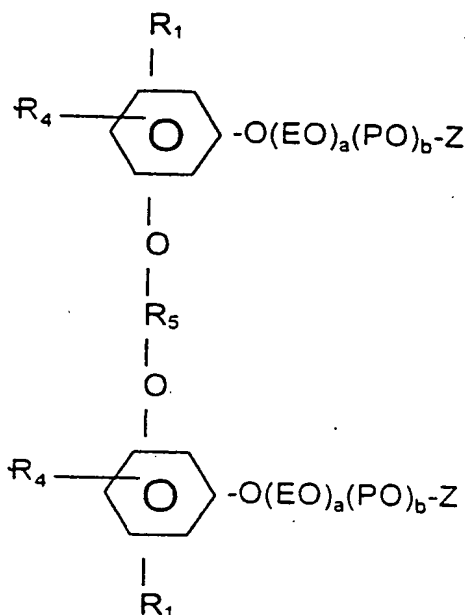
V.

20



25

VI.



wherein R_1 , R_4 , R_5 , Z , a , and b are as defined hereinbefore.

The primary hydroxyl group of these surfactants can be readily phosphated, sulfated or carboxylated by standard techniques.

The compounds included in Formula II can be prepared by a variety of synthetic routes. For instance, the compounds of Formula IV can be prepared by condensing a monoalkyl phenol with paraformaldehyde in the presence of an acid catalyst such as acetic acid. The compounds of Formula V can be synthesized by a Lewis acid catalyzed reaction of an alkylphenol with a dicarboxylic acid, e.g., terephthalic acid.

The compounds of Formula II are more fully described in copending application U.S.S.N. 60/009,075 filed 12/21/95, the entire disclosure of which is incorporated herein by reference.

A class of gemini surfactants that can be used in providing the improved emulsions which are operable at lower concentrations as

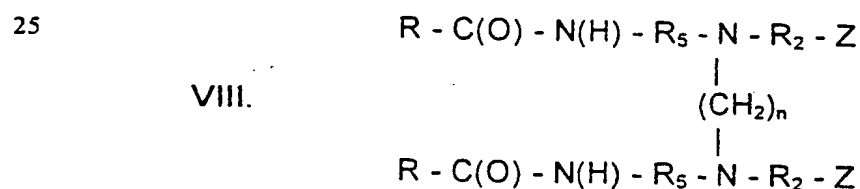
disclosed in the present invention include a group of amphoteric, and cationic quaternary surfactants comprising compounds of the formula:



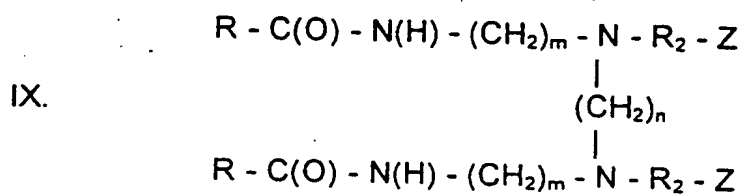
15 wherein R, t, and Z are as defined hereinbefore. R₁ is as defined before and includes the [-(EO)_a(PO)_bO-]H moiety. R₂ is as defined before, however, D includes the following moieties: -N(R₆)-C(O)-R₅-CH₂O- and -N(R₆)-C(O)-R₅-N(R₆)-R₄-. When t is zero, the compounds are amphoteric and when t is 1, the compounds are cationic quaternary

20 compounds. R₃ is selected from the group consisting of a bond, C₁-C₁₀ alkyl, and -R₈-D₁-R₈- wherein D₁, R₅, R₆, a, b, and R₈ are as defined above (except R₈ is not -OR₅O-).

Preferably, the compounds of Formula VII comprise:

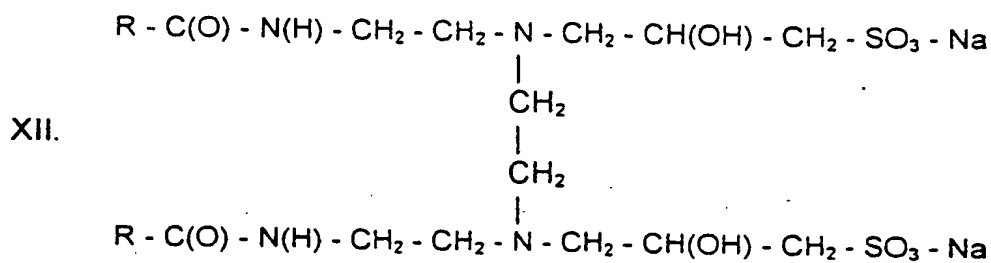
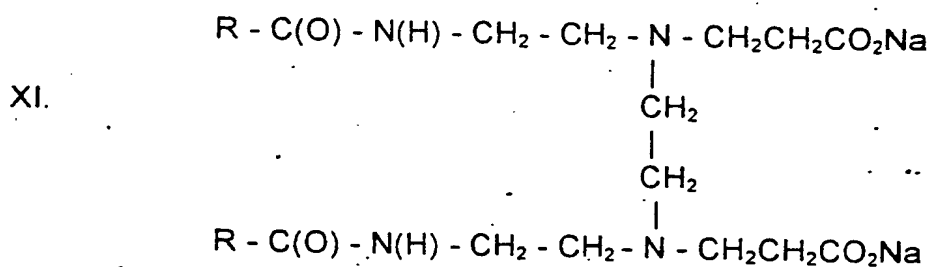
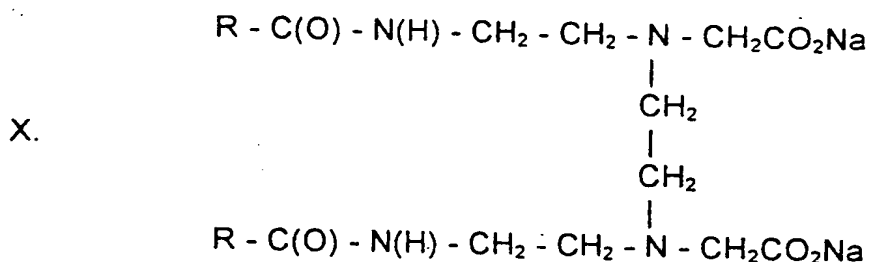


wherein R, R₂, R₅ and Z are as defined above and n equals a number from about 2 to about 10. More particularly, the compounds of Formula VII comprise:



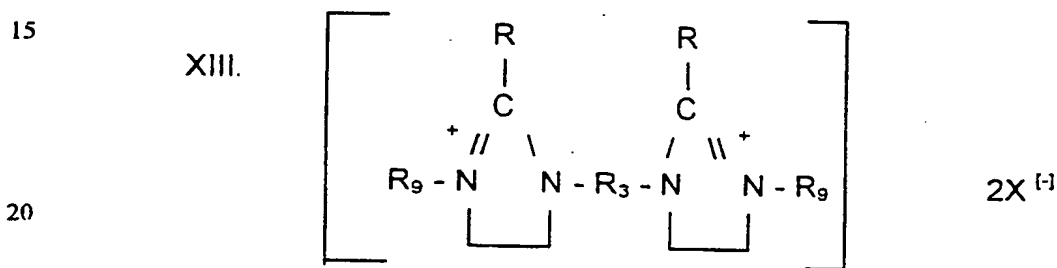
wherein R, R₂, R₅, Z, and n are as defined hereinbefore; and m independently equals a number between about 2 and about 10.

Representative compounds of Formula VII include:



While the compounds of Formulae VII - XII can be prepared by a variety of synthetic routes, it has been found that they can be produced particularly effectively by a process which utilizes a polyamine reactant having at least four amino groups of which two are terminal primary amines such as triethylene tetramine. These processes are more fully set forth in copending application "Amphoteric Surfactants Having Multiple Hydrophobic and Hydrophilic Groups", U.S.S.N. 08/292,993 filed 08/19/94, the entire disclosure of which is incorporated herein by reference.

Another group of gemini surfactants which have been found to provide the low concentration emulsions of this invention are the cyclic cationic quaternary surfactants of the formula:



wherein R and R₃ are as identified hereinbefore in formula VII; R₉ is independently a C₁ - C₁₀ alkyl or alkylaryl; and X represents a counterion such as an anion illustrated by halogen (Cl, Br, and I), alkylsulfate such as methyl or ethylsulfate, alkylphosphate such as methylphosphate, and the like.

Preferably, the compounds used in the present invention comprise those of Formula XIII in which R₃ is a C₂ - C₄ alkyl, most preferably ethyl, R₉ is a lower alkyl of from 1 to about 4 carbon atoms, most preferably methyl; and X is halogen or methylsulfate.

Also included in the gemini surfactants useful in this invention are those of the formula:



25 Some of the compounds such as those described above are set forth more fully in U.S. Patent 5,534,197 which description is incorporated herein by reference.

43

such as palm kernel oil, palm oil, osya oil, rapeseed oil, castor oil or animal fat sources such as herring oil and beef tallow. Generally, the fatty acids from natural sources in the form of the fatty acid or the triglyceride oil can be a mixture of alkyl radicals containing from about 5
5 to about 22 carbon atoms. Illustrative of the natural fatty acids are caprylic (C₈), capric (C₁₀), lauric (C₁₂), myristic (C₁₄), palmitic (C₁₆), stearic (C₁₈), oleic (C₁₈, monounsaturated), linoleic (C₁₈, diunsaturated), linolenic (C₁₈, triunsaturated), ricinoleic (C₁₈, monounsaturated) arachidic (C₂₀), gadolic (C₂₀, monounsaturated), behenic (C₂₂) and erucic (C₂₂). These
10 fatty acids can be used per se, as concentrated cuts or as fractionations of natural source acids. The fatty acids with even numbered carbon chain lengths are given as illustrative though the odd numbered fatty acids can also be used. In addition, single carboxylic acids, e.g., lauric acid, or other cuts, as suited for the particular application, may be used.

15 Where desired, the surfactants used in the present invention can be oxyalkylated by reacting the product with an alkylene oxide according to known methods, preferably in the presence of an alkaline catalyst. The free hydroxyl groups of the alkoxyated derivative can then be sulfated, phosphated or acylated using normal methods such as sulfation
20 with sulfamic acid or sulfur trioxide-pyridine complex, or acylation with an acylating agent such as a carboxylic acid, ester, and the naturally occurring triglyceride esters thereof.

For alkylation conditions and commonly used alkylating agents, see Amphoteric Surfactants Vol. 12, Ed. B. R. Bluestein and C. L. Hilton,
25 Surfactant Science Series 1982, pg. 17 and references cited therein, the disclosures of which are incorporated herein by reference.

For sulfation and phosphation, see Surfactant Science Series, Vol. 7, Part 1, S. Shore & D. Berger, page 135, the disclosure of which is incorporated herein by reference. For phosphating review, see
30 Surfactant Science Series, Vol. 7, Part II, E. Jungermann & H.

Silbertman, page 495, the disclosure of which is incorporated herein by reference.

The surfactant compositions of the invention are extremely effective in aqueous solution at low concentrations as defined herein.

- 5 The surfactants of the invention can be used in any amount needed for a particular application which can be easily determined by a skilled artisan without undue experimentation.

IV. Auxiliary Detergent Ingredients

10 A. Detergency Builders

Compositions of the present invention may include detergency builders selected from any of the conventional inorganic and organic water-soluble builder salts, including neutral or alkaline salts, as well as various water-insoluble and so-called "seeded" builders.

- 15 Builders are preferably selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, polyhydroxysulfonates, polyacetates, carboxylates, and polycarboxylates. Most preferred are the alkali metal, especially sodium, salts of the above.
- 20

- Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene-1, 1-diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid.
- 25

- Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of SiO_2 to alkali metal
- 30

oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Highly preferred polycarboxylate builders herein are set forth in U.S. Patent No. 3,308,067, Diehl, issued March 7, 1967 incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other builders include the carboxylated carbohydrates of U.S. Patent No. 3,723,322, Diehl incorporated herein by reference.

Other useful builders herein are sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate phloroglucinol trisulfonate, water-soluble polyacrylates (having molecular weights of from about 2,000 to about 200,000 for example), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent No. 4,144,226, issued March 13, 1979 to Crutchfield et al.; and U. S. Patent No. 4,246,495, issued March 27, 1979 to Crutchfield et al., both incorporated herein by reference.

"Insoluble" builders include both seeded builders such as 3:1 weight mixtures of sodium carbonate and calcium carbonate; and 2.7:1 weight mixtures of sodium sesquicarbonate and calcium carbonate.

Amphorus and crystalline alumino silicates such as hydrated sodium Zeolite A are commonly used in laundry detergent applications. They have a particle size diameter of 0.1 micron to about 10 microns depending on water content of these molecules. These are referred to as ion exchange materials. Crystalline alumino silicates are characterized by their calcium ion exchange capacity. Amphorus alumino silicates are usually characterized by their magnesium exchange capacity. They can be naturally occurring or synthetically derived.

A detailed listing of suitable detergency builders can be found in U.S. Patent No. 3,936,537, *supra*, incorporated herein by reference.

B. Miscellaneous Detergent Ingredients

Detergent composition components may also include hydrotropes, enzymes (e.g., proteases, amylases and cellulases), enzyme stabilizing agents, pH adjusting agents (monoethanolamine, sodium carbonate, etc.) halogen bleaches (e.g., sodium and potassium dichloroisocyanurates), peroxyacid bleaches (e.g., diperoxydodecane-1,12-dioic acid), inorganic percompound bleaches (e.g., sodium perborate), antioxidants as optional stabilizers, reductive agents, activators for percompound bleaches (e.g., tetraacetylenediamine and sodium nonanoyloxybenzene sulfonate), soil suspending agents (e.g., sodium carboxymethyl cellulose), soil anti-redispersion agents, corrosion inhibitors, perfumes and dyes, buffers, whitening agents, solvents (e.g., glycols and aliphatic alcohols) and optical brighteners. Any of other commonly used auxiliary additives such as inorganic salts and common salt, humectants, solubilizing agents, UV absorbers, softeners, chelating agents, static control agents and viscosity modifiers may be added to the detergent compositions of the invention.

For bar compositions, processing aids are optionally used such as salts and/or low molecular weight alcohols such as monohydric, dihydric (glycol, etc.), trihydric (glycerol, etc.), and polyhydric (polyols)

alcohols. Bar compositions may also include insoluble particulate material components, referred to as "fillers" such as calcium carbonate, silica and the like.

5 V. Composition Concentrations

The amount of the aminosilicone compound used in the compositions and methods of this invention will typically be sufficient to yield a concentration of aminosilicone compound in the washing medium of from about 0.001 to about 0.2 grams of aminosilicone compound per
10 liter of washing medium, more typically from about 0.005 to about 0.1 g/L, and even more typically from about 0.01 to about 0.04 g/L.

In the compositions of the invention, the aminosilicone compound will typically be present in an amount of from about 0.005 to about 30 % by weight, more typically from about 1 to about 10 % by weight.

15 The compositions can be in any form that is convenient for use as a detergent, e.g. bars, powders, flakes, pastes, or liquids which may be aqueous or non-aqueous and structured or unstructured. The detergent compositions can be prepared in any manner which is convenient and appropriate to the desired physical form so as co-agglomeration, spray
20 drying, or dispersing in a liquid.

The total weight percentages of the conventional surfactants of the present invention, all weight percentages being based on the total active weight of the compositions of this invention consisting of aminosilicone compound, optional carrier, conventional surfactant(s), gemini
25 surfactant(s), soil release agent(s), and (optionally) detergency builder(s) are about 10 to about 99.9 weight percent, typically about 15-75 weight percent.

The gemini surfactants are typically present, if employed, at a level of about 0.005 to about 50, typically from about 0.02-15.0, active weight
30 percent of the composition.

The polymeric soil release agents, are typically present, if employed, at a level of from about 0.05 to about 40, typically from about 0.2-15 active weight percent.

The optional detergency builders are suitably present at a level of
5 from about 0 to about 70 weight percent, typically from about 5 to about 50 weight percent.

VI. Industrial Applicability

The compositions and methods of this invention can be used to
10 clean various fabrics, e.g. wool, cotton, silk, polyesters, nylon, other synthetics, blends of multiple synthetics and or synthetic/natural fiber blends. The compositions and method are particularly useful with colored fabrics, i.e. those that have a visually perceptible hue. The compositions and methods are also particularly useful in connection with
15 washing media that also contain a fragrance. The fragrance need not be pre-mixed or pre-reacted with the aminosilicone oil in any way nor must the fragrance as an active principle a hydroxy functional compound.

The fragrance substances that may be used in the context of the invention include natural and synthetic fragrances, perfumes, scents, and
20 essences and any other substances and mixtures of liquids and/or powdery compositions which emit a fragrance. As the natural fragrances, there are those of animal origin, such as musk, civet, castreum, ambergris, or the like, and those of vegetable origin, such as lemon oil, rose oil, citronella oil, sandalwood oil, peppermint oil, cinnamon oil, or the
25 like. As synthetic fragrances, there are mixed fragrances of alpha-pinene, limonene, geraniol, linalool, lavandulol, nerolidol, or the like.

VII. Soluble Powder Detergent Compositions Without Inorganic Phosphates

For a good implementation of the invention, said compositions comprise:

- from 5 to 60%, preferably from 8 to 40%, of their weight of at least one surface-active agent (S)
- 5 - from 5 to 80%, preferably from 8 to 40%, of their weight of at least one soluble inorganic or organic builder (B)
- from 0.01 to 8%, preferably from 0.1 to 5%, very particularly from 0.3 to 3%, of their weight of at least one aminosilicone (AS).
- 10 Mention may be made, among surface-active agents, of the anionic or non-ionic surface-active agents commonly used in the field of detergents for washing laundry, such as anionic surface-active agents, such as :
 - alkyl ester sulphonates of formula $R-CH(SO_3M)-COOR'$, where R
 - 15 represents a C_{8-20} , preferably $C_{10}-C_{16}$, alkyl radical, R' a C_1-C_6 , preferably C_1-C_3 , alkyl radical and M an alkali metal (sodium, potassium or lithium) cation, a substituted or unsubstituted ammonium (methyl-, dimethyl-, trimethyl- or tetramethylammonium, dimethylpiperidinium, and the like) cation or a cation derived from an alkanolamine (monoethanolamine,
 - 20 diethanolamine, triethanolamine, and the like);
 - alkyl sulphates of formula $ROSO_3M$, where R represents a C_5-C_{24} , preferably $C_{10}-C_{18}$, alkyl or hydroxyalkyl radical, M representing a hydrogen atom or a cation with the same definition as above, and their ethoxylated (EO) and/or propoxylated (PO) derivatives exhibiting an
 - 25 average of 0.5 to 30, preferably of 0.5 to 10, EO and/or PO units;
 - alkylamide sulphates of formula $RCONHR'OSO_3M$, where R represents a C_2-C_{22} , preferably C_6-C_{20} , alkyl radical, R' a C_2-C_3 alkyl radical, M representing a hydrogen atom or a cation with the same definition as above, and their ethoxylated (EO) and/or propoxylated (PO)
 - 30 derivatives exhibiting an average of 0.5 to 60 EO and/or PO units;

- salts of C₈-C₂₄, preferably C₁₄-C₂₀, saturated or unsaturated fatty acids, C₉-C₂₀ alkylbenzenesulphonates, primary or secondary C₈-C₂₂ alkylsulphonates, alkylglycerol sulphonates, the sulphonated polycarboxylic acids described in GB-A-1,082,179, paraffin sulphonates,
- 5 N-acyl-N-alkyltaurates, alkyl phosphates, isethionates, alkylsuccinamates, alkylsulphosuccinates, the monoesters or diesters of sulphosuccinates, N-acylsarcosinates, alkylglycoside sulphates or polyethoxycarboxylates
- the cation being an alkali metal (sodium, potassium or lithium), a
- 10 substituted or unsubstituted ammonium residue (methyl-, dimethyl-, trimethyl- or tetramethylammonium, dimethylpiperidinium, and the like), or a residue derived from an alkanolamine (monoethanolamine, diethanolamine, triethanolamine, and the like);
- sophorolipids, such as those in acid or lactone form, derivatives
- 15 of 17-hydroxyoctadecenic acid; and the like.
- non-ionic surface-active agents, such as:
- polyoxyalkylenated (polyoxyethylenated, polyoxypropylenated or polyoxybutylenated) alkylphenols, the alkyl substituent of which is C₆-C₁₂, containing from 5 to 25 oxyalkylene units; mention may be made, by way
- 20 of example, of Triton X-45, X-114, X-100 or X-102, sold by Rohm & Haas Co., or Igepal NP2 to NP17 from Rhône-Poulenc;
- polyoxyalkylenated C₈-C₂₂ aliphatic alcohols containing from 1 to 25 oxyalkylene (oxyethylene or oxypropylene) units; mention may be made, by way of example, of Tergitol 15-S-9 or Tergitol 24-L-6 NMW,
- 25 sold by Union Carbide Corp., Neodol 45-9, Neodol 23-65, Neodol 45-7 or Neodol 45-4, sold by Shell Chemical Co., Kyro EOB, sold by The Procter & Gamble Co., Synperonic A3 to A9 from ICI, or Rhodasurf IT, DB and B from Rhône-Poulenc;
- the products resulting from the condensation of ethylene oxide or
- 30 of propylene oxide with propylene glycol or ethylene glycol, with a weight-

average molecular mass of the order of 2000 to 10,000, such as the Pluronics sold by BASF;

- the products resulting from the condensation of ethylene oxide or of propylene oxide with ethylenediamine, such as the Tetronics sold by
5 BASF;

- ethoxylated and/or propoxylated C₈-C₁₈ fatty acids containing from 5 to 25 oxyethylene and/or oxypropylene units;

- C₈-C₂₀ fatty acid amides containing from 5 to 30 oxyethylene units;

10 - ethoxylated amines containing from 5 to 30 oxyethylene units;

- alkoxyated amidoamines containing from 1 to 50, preferably from 1 to 25, very particularly from 2 to 20, oxyalkylene units (preferably oxyethylene units);

- amine oxides, such as (C₁₀-C₁₈ alkyl)dimethylamine oxides or (C₈-
15 C₂₂ alkoxy)ethyldihydroxyethylamine oxides;

- alkoxyated terpene hydrocarbons, such as ethoxylated and/or propoxylated a- or b-pinenes, containing from 1 to 30 oxyethylene and/or oxypropylene units;

- the alkylpolyglycosides which can be obtained by condensation
20 (for example by acid catalysis) of glucose with primary fatty alcohols (US-A-3,598,865, US-A-4,565,647, EP-A-132,043, EP-A-132,046, and the like) exhibiting a C₄-C₂₀, preferably C₈-C₁₈, alkyl group and a mean number of glucose units of the order of 0.5 to 3, preferably of the order of 1.1 to 1.8, per mole of alkylpolyglycoside (APG); mention may in
25 particular be made of those exhibiting:

- a C₈-C₁₄ alkyl group and, on average, 1.4 glucose units per mole

- a C₁₂-C₁₄ alkyl group and, on average, 1.4 glucose units per mole

- a C₈-C₁₄ alkyl group and, on average, 1.5 glucose units per mole

- a C₈-C₁₀ alkyl group and, on average, 1.6 glucose units per mole sold respectively under the names Glucocon 600 EC®, Glucocon 600 CSUP®, Glucocon 650 EC® and Glucocon 225 CSUP® by Henkel.

Mention may particularly be made, among soluble inorganic builders (B), of:

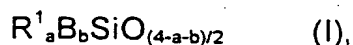
- amorphous or crystalline alkali metal silicates of formula $x\text{SiO}_2 \cdot \text{M}_2\text{O} \cdot y\text{H}_2\text{O}$, with $1 \leq x \leq 3.5$ and $0 \leq y/(x+1+y) \leq 0.5$, where M is an alkali metal and very particularly sodium, including lamellar alkali metal silicates, such as those described in US-A-4,664,839;
- alkaline carbonates (bicarbonates, sesquicarbonates);
- cogranules of hydrated alkali metal silicates and of alkali metal carbonates (sodium or potassium) which are rich in silicon atoms in the Q2 or Q3 form, described in EP-A-488,868; and
- tetraborates or borate precursors.

Mention may particularly be made, among soluble organic builders (B), of:

- water-soluble polyphosphonates (ethane-1-hydroxy-1,1-diphosphonates, salts of methylenediphosphonates, and the like);
- water-soluble salts of carboxyl polymers or copolymers, such as the water-soluble salts of polycarboxylic acids with a molecular mass of the order of 2000 to 100,000 obtained by polymerization or copolymerization of ethylenically unsaturated carboxylic acids, such as acrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid, mesaconic acid, citraconic acid or methylenemalononic acid, and very particularly polyacrylates with a molecular mass of the order of 2000 to 10,000 (US-A-3,308,067) or copolymers of acrylic acid and of maleic anhydride with a molecular mass of the order of 5000 to 75,000 (EP-A-066,915);
- polycarboxylate ethers (oxydisuccinic acid and its salts, tartrate monosuccinic acid and its salts, tartrate disuccinic acid and its salts);

- hydroxypolycarboxylate ethers;
- citric acid and its salts, mellitic acid, succinic acid and their salts;
- salts of polyacetic acids (ethylenediaminetetraacetates, nitrilotriacetates, N-(2-hydroxyethyl)nitrilodiacetates);
- 5 - (C₅-C₂₀ alkyl)succinic acids and their salts (2-dodecenylsuccinates, laurylsuccinates, and the like);
- polyacetal carboxylic esters;
- polyaspartic acid, polyglutamic acid and their salts;
- polyimides derived from the polycondensation of aspartic acid
- 10 and/or of glutamic acid;
- polycarboxymethylated derivatives of glutamic acid (such as N,N-bis(carboxymethyl)glutamic acid and its salts, in particular the sodium salt) or of other amino acids; and
- aminophosphonates, such as nitrilotris(methylenephosphonate)s.

15 For a good implementation of the invention, the said aminosilicone (AS) can be chosen from the aminopolyorganosiloxanes (APS) comprising siloxane units of general formulae:



where $a+b = 3$, with $a = 0, 1, 2$ or 3 and $b = 0, 1, 2$ or 3



where $c+d = 2$, with $c = 0$ or 1 and $d = 1$ or 2



where $e+f = 0$ or 1 , with $e = 0$ or 1 and $f = 0$ or 1

25 in which formulae,

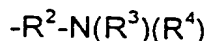
- the R^1 symbols, which are identical or different, represent a saturated or unsaturated, linear or branched, aliphatic radical containing from 1 to 10 carbon atoms or a phenyl radical, optionally substituted by fluoro or cyano groups;

- the A symbols, which are identical or different, represent a primary, secondary, tertiary or quaternized amino group bonded to the silicon via an SiC bond;
- the B symbols, which are identical or different, represent
- 5 - an OH functional group;
- an OR functional group, where R represents an alkyl group containing from 1 to 12 carbon atoms, preferably from 3 to 6 carbon atoms, very particularly 4 carbon atoms;
- an OCOR' functional group, where R' represents an alkyl group
- 10 containing from 1 to 12 carbon atoms, preferably 1 carbon atom; or
- the A symbol.

The said aminopolyorganosiloxanes (APS) preferably comprise units of formula (I), (II), (III) and optionally (IV), where

- in the units of formula (I), a = 1, 2 or 3 and b = 0 or 1 and
- 15 - in the units of formula (II), c = 1 and d = 1.

The said A symbol is preferably an amino group of formula



where

- the R² symbol represents an alkylene group containing from 2 to
- 20 6 carbon atoms, which group is optionally substituted or interrupted by one or more nitrogen or oxygen atoms,
- the R³ and R⁴ symbols, which are identical or different, represent
- H,
- an alkyl or hydroxyalkyl group containing from 1 to 12 carbon
- 25 atoms, preferably from 1 to 6 carbon atoms,
- an aminoalkyl group, preferably a primary aminoalkyl group, the alkyl group of which contains from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, which group is optionally substituted and/or interrupted by at least one nitrogen and/or oxygen atom, the said amino

group optionally being quaternized, for example by a hydrohalic acid or an alkyl or aryl halide.

Mention may particularly be made, as example of A symbol, of those of formulae:

- 5 $-(\text{CH}_2)_3\text{NH}_2$; $-(\text{CH}_2)_3\text{NH}_3^+ \text{X}^-$;
 $-(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$; $-(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2(\text{C}_{18}\text{H}_{37}) \text{X}^-$;
 $-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$; $-(\text{CH}_2)_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$; and
 $-(\text{CH}_2)_3\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$.

10 Among these, the preferred formulae are:

$$-(\text{CH}_2)_3\text{NH}_2 \quad -(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2 \text{ and } -(\text{CH}_2)_3\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2.$$

The R¹ symbol preferably represent methyl, ethyl, vinyl, phenyl, trifluoropropyl or cyanopropyl groups. It very particularly represents the methyl group (at least predominantly).

15 The B symbol preferably represents an OR group where R contains from 1 to 6 carbon atoms, very particularly 4 carbon atoms, or the A symbol. The B symbol is very preferably a methyl or butoxy group.

The aminosilicone is preferably at least substantially linear. It is very preferably linear, that is to say does not contain units of formula (IV).

20) It can exhibit a number-average molecular mass of the order of 2000 to 50,000, preferably of the order of 3000 to 30,000.

For a good implementation of the invention, said aminosilicones (AS) or the aminopolyorganosiloxanes (APS) can exhibit in their chain, per total of 100 silicon atoms, from 0.1 to 50, preferably from 0.3 to 10, very particularly from 0.5 to 5, aminofunctionalized silicon atoms.

Insoluble inorganic builders can additionally be present but in a limited amount, in order not to exceed the level of less than 20% of insoluble inorganic material defined above.

Mention may be made, among these adjuvants, of crystalline or amorphous aluminosilicates of alkali metals (sodium or potassium) or of ammonium, such as zeolites A, P, X, and the like.

The said detergent compositions can additionally comprise
5 standard additives for powder detergent compositions, such as soil release agents in amounts of the order of 0.01-10%, preferably of the order of 0.1 to 5% and very particularly of the order of 0.2-3% by weight, agents such as:

- 10 - cellulose derivatives, such as cellulose hydroxyethers, methylcellulose, ethylcellulose, hydroxypropyl methylcellulose or hydroxybutyl methylcellulose;
- poly(vinyl ester)s grafted onto polyalkylene stems, such as poly(vinyl acetate)s grafted onto polyoxyethylene stems (EP-A-219,048);
- 15 - poly(vinyl alcohol)s;
- polyester copolymers based on ethylene terephthalate and/or propylene terephthalate and polyoxyethylene terephthalate units, with an ethylene terephthalate and/or propylene terephthalate (number of units)/polyoxyethylene terephthalate (number of units)
20 molar ratio of the order of 1/10 to 10/1, preferably of the order of 1/1 to 9/1, the polyoxyethylene terephthalates exhibiting polyoxyethylene units having a molecular weight of the order of 300 to 5000, preferably of the order of 600 to 5000 (US-A-3,959,230, US-A-3,893,929, US-A-4,116,896, US-A-4,702,857 and US-A-
25 4,770,666);
- sulphonated polyester oligomers, obtained by sulphonation of an oligomer derived from ethoxylated allyl alcohol, from dimethyl terephthalate and from 1,2-propanediol, exhibiting from 1 to 4 sulphonate groups (US-A-4,968,451);

- polyester copolymers based on propylene terephthalate and polyoxyethylene terephthalate units which are optionally sulphonated or carboxylated and terminated by ethyl or methyl units (US-A-4,711,730) or optionally sulphonated polyester oligomers terminated by alkylpolyethoxy groups (US-A-4,702,857) or anionic sulphopolyethoxy (US-A-4,721,580) or sulphoaroyl (US-A-4,877,896) groups;
 - sulphonated polyesters with a molecular mass of less than 20,000, obtained from a diester of terephthalic acid, isophthalic acid, a diester of sulphisophthalic acid and a diol, in particular ethylene glycol (WO 95/32997);
 - polyesterpolyurethanes obtained by reaction of a polyester with a number-average molecular mass of 300 to 4000, obtained from adipic acid and/or terephthalic acid and/or sulphisophthalic acid and a diol, with a prepolymer containing end isocyanate groups obtained from a poly(ethylene glycol) with a molecular mass of 600-4000 and a diisocyanate (FR-A-2,334,698);
- anti-redeposition agents, in amounts of approximately 0.01-10% by weight for a powder detergent composition and of approximately 0.01-5% by weight for a liquid detergent composition, agents such as:
- ethoxylated monoamines or polyamines or ethoxylated amine polymers (US-A-4,597,898, EP-A-011,984);
 - carboxymethylcellulose;
 - sulphonated polyester oligomers obtained by condensation of isophthalic acid, dimethyl sulphosuccinate and diethylene glycol (FR-A-2,236,926); and
 - polyvinylpyrrolidones;

bleaching agents, in an amount of approximately 0.1-20%, preferably 1-10%, of the weight of the said powder detergent composition, such as:

- perborates, such as sodium perborate monohydrate or tetrahydrate;
- peroxygenated compounds, such as sodium carbonate peroxohydrate, pyrophosphate peroxohydrate, urea hydrogen peroxide, sodium peroxide or sodium persulphate;
- 5 - percarboxylic acids and their salts (known as "percarbonates"), such as magnesium monoperoxyphthalate hexahydrate, magnesium meta-chloroperbenzoate, 4-nonylamino-4-oxoperoxybutyric acid, 6-nonylamino-6-oxoperoxy-caproic acid, diperoxydodecanedioic acid, peroxysuccinic acid nonylamide or decyldiperoxysuccinic acid,
- 10 preferably in combination with a bleaching activator generating, in situ in the washing liquor, a peroxycarboxylic acid; mention may be made, among these activators, of tetraacetylenediamine, tetraacetylmethylenediamine, tetraacetyl glycoluril, sodium p-acetoxybenzenesulphonate, pentacetyl glucose, octaacetyl lactose, and
- 15 the like;
- fluorescence agents, in an amount of approximately 0.05-1.2% by weight, agents such as derivatives of stilbene, pyrazoline, coumarin, fumaric acid, cinnamic acid, azoles, methinecyanines, thiophenes, and the like;
- foam-suppressant agents, in amounts which can range up to 5% by
- 20 weight, agents such as:
 - C₁₀-C₂₄ fatty monocarboxylic acids or their alkali metal, ammonium or alkanolamine salts or fatty acid triglycerides;
 - saturated or unsaturated, aliphatic, alicyclic, aromatic or heterocyclic hydrocarbons, such as paraffins or waxes;
 - 25 - N-alkylaminotriazines;
 - monostearyl phosphates or monostearyl alcohol phosphates; and
 - polyorganosiloxane oils or resins, optionally combined with silica particles;
- softeners, in amounts of approximately 0.5-10% by weight, agents such
- 30 as clays (smectites, such as montmorillonite, hectorite or saponite);

enzymes, in an amount which can range up to 5 mg by weight, preferably of the order of 0.05-3 mg, of active enzyme/g of detergent composition, enzymes such as proteases, amylases, lipases, cellulases or peroxydases (US-A-3,553,139, US-A-4,101,457, US-A-4,507,219 and
5 US-A-4,261,868) and other additives, such as:

- alcohols (methanol, ethanol, propanol, isopropanol, propanediol, ethylene glycol or glycerol);
- buffer agents or fillers, such as sodium sulphate or alkaline earth metal carbonates or bicarbonates; and
- 10 - pigments,

the amounts of optional insoluble inorganic additives having to be sufficiently limited in order not to exceed the level of less than 20% of insoluble inorganic materials defined above.

The present invention is further illustrated by the following
15 examples, provided that no observations or other statements made therein should be construed to limit the invention, unless otherwise expressly indicated in the claims appended hereto. All amounts, parts, percentages, and ratios expressed in this specification, including the claims are by weight unless otherwise apparent in context.

20

Examples

Washing Procedure

All washes were completed in a washing machine (a US model of Whirlpool Co.) commercially available for household use using an 18
25 minute regular wash cycle. After each wash, the fabric samples were dried in dryer (a KENMORE brand dryer commercially available from Sears & Roebuck, Co). for household use for 30 minutes on the dryer setting for cotton fabrics.

Tapwater at 80°F (30 ppm hardness) was used to fill the washing
30 machine. Additional water hardness was added by a Repipet dispenser

to deliver 100 ppm of additional hardness for a total washing medium hardness of 130 ppm. The water was agitated to ensure that the final washwater temperature was correct. A powdered or liquid detergent formulation was then added followed at the concentration shown below for each formulation. After agitating the washwater (total 45 L) for 30 seconds, an aminosilicone compound was added to the washing medium to obtain an aminosilicone content in the washwater as shown below. In those instances wherein a clay was added to the washing medium, the aminosilicone compound and a bentonite clay having a high montmorillonite content and a low cristobalite and quartz content was pre-mixed with the silicone compound so as to form an agglomerate. The washwater was then agitated to ensure mixing of the components. Fabric in the form of swatches and/or clothing was added last. The wash was agitated for an additional 30 seconds to ensure wetting of the fabrics and then the wash cycle was reset to 18 minutes and a wash/rinse cycle was completed. The loads were occasionally rotated through four identical washing machines to mitigate any differences in washing activity of the four machines (e.g. speed of agitation). Prior to rotation, the washing machines were thoroughly rinsed. In each wash series, a control wash (i.e. detergent with no aminosilicone additive) was performed. It is noted that in all the examples, all like ingredient abbreviations or designations indicate like ingredients.

Detergent Formulations

The detergent formulations used are set forth below.

Detergent Formulation A:

A non-Phosphate mixed surfactant (anionic and nonionic) Heavy Duty Detergent (HDD) powder sold in the US by USA Detergents as Xtra-Detergent, which contains 10.5 % silicate, 12 % linear

alkylbenzenesulfonate (LAS), 2 % nonionic--alcohol ethoxylate, 40 % Na carbonate, optical brightener, sodium sulfate, and perfume. This detergent formulation was used at 1.2 g Xtra deter/liter wash water.

5 Detergent Formulation B:

A phosphate, all anionic HDD powder brand sold by Colgate in Columbia which contains 15 % Phosphate (TPP) 25 % LAS. 5 % Na Silicate, and 30 % Na sulfate. This detergent formulation was used at 3 g/L washwater.

10

Detergent Formulation C:

An anionic/nonionic Super Concentrated Heavy Duty Liquid (3/8 Cup) sold in the US by Lever Bros. as Wisk Liquid which contains LAS, ether sulfate, nonionic-- alcohol ethoxylate, citrate, perfume, enzymes,
15 enzyme stabilizer, optical brightener and buffer system. This detergent formulation was used at 1.2 g/L.

Detergent Formulation D:

A non-Phosphate, zeolite-containing Super Concentrated Heavy
20 Duty Detergent (SCHDD) powder mixed nonionic/anionic system sold in the US as Fab Powder in which nonionic:anionic ratio is > 1 (for the other liquid and powder detergents: nonionic: anionic ratio is < 1) which contains 20 % Zeolite, 10 % Nonionic surfactant, 2 % Anionic surfactant, 30 % sodium carbonate, 5 % sodium citrate, 0.0 - 0.3 % perfume, 0.0 - 3
25 % enzymes, 0.2 - 0.3 % brightener. 0.01 - 2 % anti-redeposition agents, and 2-3 % polyacrylate. A fragrance (Fresh Floral from International Flavors and Fragrances) was post added: at 0.2 % level, detergent was allowed to "age" 1 week at room temperature with occasionally stirring/shaking each day before it was used This detergent formulation
30 was used at 1.0 g/L.

Fabric/Clothing:

The clothing and fabric used were purchased at consumer retail. To ensure uniformity amongst the products tested; the clothing articles were evenly divided amongst the products. For each detergent product
5 2-4 replicates of each clothing /fabric type are added to the wash. Fabric Types: cotton lycra (95 %/ 5 %); corduroy; 100 % cotton knit--single and double; 100 % cotton weave; cotton polyester blends, cotton synthetic blends; cotton terry cloth towels; and flannel. The colors of the clothing and fabrics varied.

10

Example 1

The general procedure set forth above was accomplished with an aminosilicone compound of formula I wherein R^1 and R^8 are methoxy, R^2 , R^3 , R^4 , R^5 , R^6 , R^9 , and R^{10} are methyl, R^7 is N-aminoethyl-3-aminopropyl,
15 m is about 135, and n is about 1.5 (0.42% Nitrogen; viscosity of 300 m.pa.s). The amount of aminosilicone compound was sufficient to present a concentration of 0.04 g/L of washing medium.

Example 2

20 The general procedure set forth above was accomplished with an aminosilicone compound of formula I wherein R^1 and R^8 are methoxy, R^2 , R^3 , R^4 , R^5 , R^6 , R^9 , and R^{10} are methyl, R^7 is N-aminoethyl-3-aminopropyl, m is about 135, and n is about 1.5 (0.42% Nitrogen; viscosity of 300 m.pa.s). The amount of aminosilicone compound was sufficient to
25 present a concentration of 0.02 g/L of washing medium.

Example 3

The general procedure set forth above was accomplished with an aminosilicone compound of formula I wherein R^1 and R^8 are methoxy, R^2 ,
30 R^3 , R^4 , R^5 , R^6 , R^9 , and R^{10} are methyl, R^7 is N-aminoethyl-3-aminopropyl,

m is about 270, and n is about 1.5 (0.21% Nitrogen; viscosity of 1000 m.pa.s). The amount of aminosilicone compound was sufficient to present a concentration of 0.04 g/L of washing medium.

5

Example 4

The general procedure set forth above was accomplished with an aminosilicone compound of formula I wherein R¹ and R⁸ are methoxy, R², R³, R⁴, R⁵, R⁶, R⁹, and R¹⁰ are methyl, R⁷ is N-aminoethyl-3-aminopropyl, m is about 270, and n is about 1.5 (0.21% Nitrogen; viscosity of 1000 m.pa.s). The amount of aminosilicone compound was sufficient to present a concentration of 0.02 g/L of washing medium.

10

Example 5

The general procedure set forth above was accomplished with an aminosilicone compound of formula I wherein R¹ and R⁸ are ethoxy, R², R³, R⁴, R⁵, R⁶, R⁹, and R¹⁰ are methyl, R⁷ is 3-aminopropyl, m is about 135, and n is about 1.5 (0.21% Nitrogen; viscosity of 300 m.pa.s). The amount of aminosilicone compound was sufficient to present a concentration of 0.04 g/L of washing medium.

15

Example 6

The general procedure set forth above was accomplished with an aminosilicone compound of formula I wherein R¹ and R⁸ are methoxy, R², R³, R⁴, R⁵, R⁶, R⁹, and R¹⁰ are methyl, R⁷ is 3-aminopropyl, m is about 135, and n is about 1.5 (0.21% Nitrogen; viscosity of 300 m.pa.s). The amount of aminosilicone compound was sufficient to present a concentration of 0.02 g/L of washing medium.

20

Studies

General Procedure: A panel comprised of at least 10 experienced evaluators compares the washed swatches/clothing one of which is washed by a control detergent composition and the other of which are washed using a silicone containing "caretergent". Identical articles from each of the detergent compositions are evaluated by ranking them. All swatches/clothing articles are evaluated for color protection, brightness/intensity of colors and drape of the cloth. The swatches/clothing articles were also evaluated for softness. Again, in this test, the panelist were asked to rank the products from least to most soft.

10

Panelist evaluation of Color Protection, Softness and Drape:

Study 1

Washing Medium C had Detergent Formulation C (Wisk Liquid) alone (control).

15 Washing Medium B had Detergent Formulation C (Wisk Liquid) plus an aminosilicone not within formula 1 at 0.025 g/L.

Washing Medium A Detergent Formulation C (Wisk Liquid) plus the aminosilicone of Example 1 at 0.07 g/L .

20 **Data:**

Number of panelists: 10

Number of different types of swatches evaluated by panelist: 6

highest possible score = 60 (5 x 12)

25 **Results:**

Number of swatches washed in A which the panelist ranked as having the best:

color protection : 60

drapability of the cloth: 54

softness: 56

Number of swatches washed in B which the panelist ranked as having the best:

5 drapability of the cloth: 6
 softness: 4
 drape: 0
 softness: 0

10 *Number of swatches washed in B which the panelist ranked as having the second best:*

 color protection: 45
 drapability: 42
 softness: 33

15

Number of swatches washed in C which the panelist ranked as having the second best:

 color protection: 15
 drapability: 12
20 softness: 23

Conclusion: The addition of silicone, particularly, the addition of the silicone of Example 1 at 0.07 g/L shows significant difference in the aforementioned care benefits when compared to the control, Wisk without
25 silicone additives.

Study 2

Washing Medium C had Detergent Formulation A (X-tra) alone (control).

Washing Medium B had Detergent Formulation A (X-tra) plus the
30 aminosilicone of Example 1 at 0.04 g/L

Washing Medium A had Detergent Formulation A (X-tra) plus the aminosilicone of Example 1 0.07 g/L

Data:

5 **Part A: Color Protection:**

Number of panelists: 12

Number of different types of swatches evaluated by panelist: 5

highest possible score = 60 (5 x 12)

10 **Results:**

Number of swatches washed in A which the panelist ranked as having the best:

color protection : 54

15 *Number of swatches washed in B which the panelist ranked as having the best:*

color protection: 6

Number of swatches washed in C which the panelist ranked as having the best:

color protection: 0

20

Number of swatches washed in A which the panelist ranked as having the second best:

color protection: 6

25 *Number of swatches washed in B which the panelist ranked as having the second best:*

color protection 54

Number of swatches washed in C which the panelist ranked as having the second best:

color protection 0

Part B Softness -- two different types of towels, one fleece type clothing item, sleeve of a corduroy shirt, heavy double knit cotton swatch:

Number of panelists: 12

Number of different types of swatches evaluated by panelist: 5

5 Highest possible score = 60 (5 x 12)

Results:

Number of swatches washed in A which the panelist ranked as having the best softness: 56

10

Number of swatches washed in B which the panelist ranked as having the best softness: 4

15 *Number of swatches washed in A which the panelist ranked as having the second best softness: 4*

Number of swatches washed in B which the panelist ranked as having the second best softness: 56

20 **Conclusion:** The addition of silicone to a typical non-P US powder detergent where the silicone concentrations in the washwater ranges from 0.04 - 0.07 g/L, gives color protection and softness benefits when compared to the powder detergent without additive. At the higher silicone concentration, the softness and color protection benefits are enhanced.

25

Panelist Evaluation of Fragrance Retention:

In the cases where the garments/swatches were washed with detergents containing perfume (Wisk Liquid and US FAB basebead + 0.2
30 % perfume), a fragrance retention panel test was also completed. The

panelists are asked to determine which bundle of clothing after being dryer-dried smells the most and to describe the fragrance.

Study 1

- 5 Washing Medium C had Detergent Formulation C (Wisk Liquid) alone- (control).

Washing Medium A had Detergent Formulation C (Wisk Liquid) plus the aminosilicone of Example 1 at 0.07 g/L.

10 Data:

Number of panelists: 10

Highest possible vote: 10

Clothing bundle washed and dried 15 times. Panelist evaluated fragrance retention after the 15th dryer drying.

- 15 Highest possible score = 10

Garments washed in product A smelled the most: 10

Garments washed in product C smelled the most: 0

Study 2

- 20 Washing Medium C had Detergent Formulation D (US Fab SCHDD powder) alone (control).

Washing Medium B had Detergent Formulation D (US Fab SCHDD powder) plus the aminosilicone of Example 1 at 0.06 g/L.

- 25 Washing Medium A had Detergent Formulation D (US Fab SCHDD powder) plus the aminosilicone of Example 1 at 0.06 g/L 21637, plus 0.15 g/L bentonite clay as described above.

Number of panelists: 11

Highest possible vote: 11

Clothing bundle washed and dried 13 times. Panelist evaluated fragrance retention after the 13th dryer drying.

Garments washed in product A smelled the most: 7

Garments washed in product B smelled the most: 4

5 Garments washed in product C smelled the most: 0

Conclusion: Garments washed in a detergent containing silicone showed significant fragrance retention over detergent alone. Despite the fact that the presence of clay in a detergent formula may sometimes
10 require the use of higher fragrance concentration to overcome the absorptive nature of the clay filler, the addition of clay to the above detergent/silicone system did significantly alter the fragrance retention benefit. The garments washed in the detergent powder containing clay
15 retention than the detergent without any additives.

Panelist Evaluation of Static Control:

Static control is determined right after the clothes are dried for the
20 specific time. The panelists are asked to pull out specific swatches from the dryer and assess the clinginess/static buildup of the specific swatch to the rest of the clothing bundle, and to the dryer wall itself. In the latter case the swatch is placed on the inside vertical portion of the dryer wall; its ability to drop off the wall is observed. The static control of the
25 swatches for each of the products are ranked from most to least "clingy"/static. In this case "ties" were allowed.

Study 1

Washing Medium C had Detergent Formulation B (Colombian Fab HDD powder) alone (control)

Washing Medium B had Detergent Formulation B (Colombian Fab) plus the aminosilicone of Example 1 at 0.06 g/L

- 5 Washing Medium A had Detergent Formulation B (Colombian Fab) plus the aminosilicone of Example 1 at 0.06 g/L plus 0.3 g/L bentonite clay as described above.

Number of panelists: 5

- 10 Clothing bundle washed and dried 10 times. Panelists evaluated the static control

Most static, most clinginess - C : 5 votes

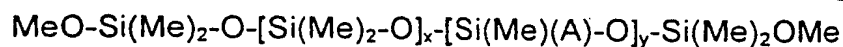
Least static, least clinginess - B equal to A : 5 votes

- 15 **Soluble Powder Detergents Without Inorganic Phosphates**

Examples 7 and 8

Two examples of detergent compositions according to the invention appear in the appended Table.

- 20 The aminosilicone employed is the aminopolydimethylsiloxane of formula:



where

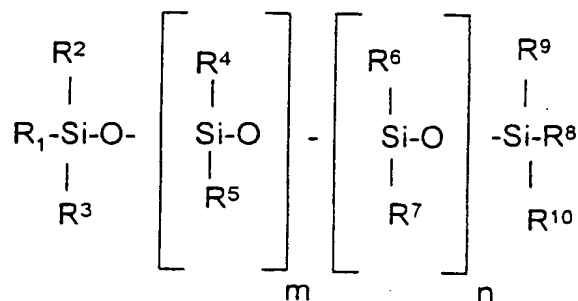
- x is equal to 135 and y to 1.5
25 - A represents the $-(\text{CH}_2)_3\text{-NH-(CH}_2)_2\text{-NH}_2$ group
- Me represents the methyl group

Table

Constituents	Formulation	
	A	B
Zeolite 4A	17	15
Nabion silicate/carbonate coganule	0	30
Silicate, $2\text{SiO}_2 \cdot \text{Na}_2\text{O}$	13	0
Sodium carbonate	15	0
Acrylate/maleate copolymer Sokalan CP5	5	5
Sodium sulphate	8.5	8.5
CMC, Blanose 7MXF	1	1
Perborate monohydrate	15	15
TAED granule	5	5
Anionic surfactant LABS Nansa	6	6
Non-ionic surfactant, Synperonic A3 (3EO ethoxylated alcohol)	3	3
Non-ionic surfactant, Synperonic A9 (9EO ethoxylated alcohol)	9	9
Enzymes (esperases, amylases, cellulase, protease)	0.5	0.5
Aminosilicone	2.0	2.0

WHAT IS CLAIMED IS:

1. A method comprising washing a colored fabric article in a washing medium comprised of a major amount by weight of water, a first minor amount by weight of a detergent and a second minor amount by weight of an aminosilicone compound having the formula:



wherein:

- 10 R^1 and R^8 are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically C_1-C_4) and alkoxy (typically C_1-C_4), R^2 , R^3 , R^9 , and R^{10} are independently selected from the group consisting of alkyl (typically C_1-C_4), and alkoxy (typically C_1-C_4), provided that one of R^2 , R^3 , R^9 , and R^{10} may be selected from the group consisting of a
- 15 primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),
- R^4 , R^5 , and R^6 are independently selected from the group consisting of
- 20 alkyl (typically C_1-C_4) and aryl (typically phenyl), R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and

m and n are numbers wherein m is greater than n (typically the ratio of m:n is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of 10 to 100,000 cps at 25° (typically the sum of n and m is from about 10 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275),

wherein said first minor amount by weight is greater than said second minor amount by weight.

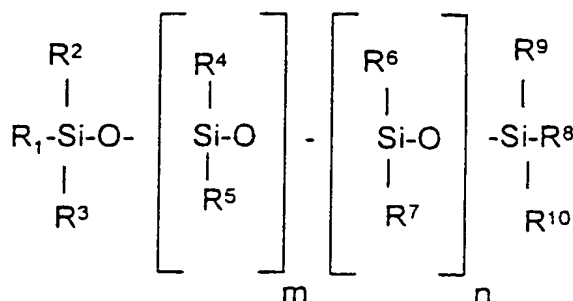
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2. A method as claimed in claim 1 wherein said washing medium is the product of mixing water with a composition comprised of said aminosilicone compound in association with an insoluble support.

15 3. A method as claimed in claim 1 wherein R¹ and R⁸ are each alkoxy.

4. A method as claimed in claim 1 wherein said washing is repeated successively with at least about ten successive washing media and
20 wherein said washing medium is effective to prevent fading of the color of said fabric after said washings.

5. A method comprising washing a fabric article in a washing medium comprised of a major amount by weight of water, a first minor amount by weight of a detergent, a second minor amount by weight of an
25 aminosilicone compound having the formula:



wherein:

- R^1 and R^8 are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically $\text{C}_1\text{-C}_4$) and alkoxy (typically $\text{C}_1\text{-C}_4$), R^2 , R^3 , R^9 , and R^{10} are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$), and alkoxy (typically $\text{C}_1\text{-C}_4$), provided that one of R^2 , R^3 , R^9 , and R^{10} may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality), R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$) and aryl (typically phenyl), R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and m and n are numbers wherein m is greater than n (typically the ratio of $m:n$ is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of 10 to 100,000 cps at 25° (typically the sum of n and m is from about 10 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275),

and a third minor amount by weight of a fragrance, wherein said first minor amount by weight is greater than each of said second minor amount by weight and said third minor amount by weight.

5 6. A method as claimed in claim 5 wherein said washing medium is the product of mixing water with a composition comprised of said aminosilicone compound in association with an insoluble support.

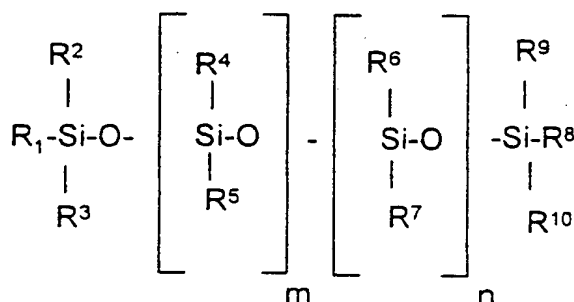
7. A method as claimed in claim 5 wherein R^1 and R^8 are each
10 alkoxy.

8. A method as claimed in claim 5 wherein said washing medium is effective to prolong the release of said fragrance from said fabric article after said washing.

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9. Usage, as a color protective agent, fragrance retainer on textiles, resistant to wear and tear, in laundry detergent compositions, of an aminosilicone compound of formula:

20



wherein:

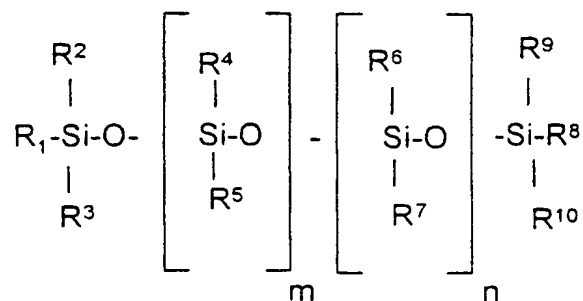
R^1 and R^8 are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically C_1 - C_4) and alkoxy (typically C_1 - C_4),

R^2 , R^3 , R^9 , and R^{10} are independently selected from the group consisting of alkyl (typically C_1 - C_4), and alkoxy (typically C_1 - C_4), provided that one of R^2 , R^3 , R^9 , and R^{10} may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality), R^4 , R^5 , and R^6 are independently selected from the group consisting of alkyl (typically C_1 - C_4) and aryl (typically phenyl), R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and

m and n are numbers wherein m is greater than n (typically the ratio of m:n is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of 10 to 100,000 cps at 25° (typically the sum of n and m is from about 10 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275).

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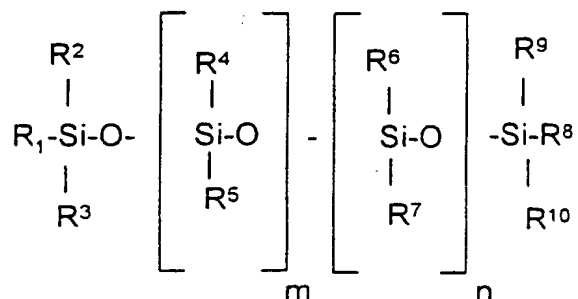
10. A detergent composition comprising a major amount by weight of a detergent and a first minor amount by weight of an aminosilicone compound having the formula:



wherein:

R¹ and R⁸ are independently alkoxy (typically C₁-C₄), R², R³, R⁹, and R¹⁰ are independently selected from the group consisting of alkyl (typically C₁-C₄), and alkoxy (typically C₁-C₄), provided that one of R², R³, R⁹, and R¹⁰ may be selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality), R⁴, R⁵, and R⁶ are independently selected from the group consisting of alkyl (typically C₁-C₄) and aryl (typically phenyl), R⁷ is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and
m and n are numbers wherein m is greater than n (typically the ratio of m:n is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of 10 to 100,000 cps at 25° (typically the sum of n and m is from about 10 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275),
and a second minor amount by weight of an insoluble support, wherein said aminosilicone compound is in association with said insoluble support.

11. A method comprising washing a fabric article in a washing medium comprised of a major amount by weight of water and a first minor amount by weight of a detergent, a second minor amount by weight of an aminosilicone compound having the formula:



wherein:

- 5 R^1 and R^8 are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically $\text{C}_1\text{-C}_4$) and alkoxy (typically $\text{C}_1\text{-C}_4$), R^2 , R^3 , R^9 , and R^{10} are independently selected from the group consisting of alkyl (typically $\text{C}_1\text{-C}_4$), and alkoxy (typically $\text{C}_1\text{-C}_4$), provided that one of R^2 , R^3 , R^9 , and R^{10} may be selected from the group consisting of a
- 10 primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),
- R^4 , R^5 , and R^6 are independently selected from the group consisting of
- 15 alkyl (typically $\text{C}_1\text{-C}_4$) and aryl (typically phenyl), R^7 is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an amino-alkyl-substituted alkyl group such that the compound will have both primary and secondary amine functionality), and
- 20 m and n are numbers wherein m is greater than n (typically the ratio of m:n is from about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of 10 to 100,000 cps at 25° (typically the sum of n and m is from about 10 to about

600, more typically from about 50 to about 400 and most typically from about 135 to about 275),

and a third minor amount by weight of an insoluble support, wherein said aminosilicone compound is in association with said insoluble support,
5 and wherein said first minor amount is greater than each of said second minor amount and said third minor amount.

12. A method as claimed in claim 11 wherein said fabric article is a colored fabric article.

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13. A method as claimed in claim 11 wherein said detergent composition is further comprised of a fragrance in a minor amount by weight.

15 14. Powder detergent compositions, without inorganic phosphates, comprising:

- at least one surface-active agent (S)
- at least one inorganic or organic builder (B) which is soluble in the washing liquor
- 20 - and at least one aminosilicone (AS),

the said compositions not comprising more than 20% of their weight of inorganic substances which are insoluble in the washing liquor.

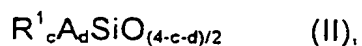
15. Compositions according to Claim 14, characterized in that they comprise:

- 25 - from 5 to 60%, preferably from 8 to 40%, of their weight of at least one surface-active agent;
- from 5 to 80%, preferably from 8 to 40%, of their weight of at least one soluble inorganic or organic builder (B);
- from 0.01 to 8%, preferably from 0.1 to 5%, very particularly from
30 0.3 to 3%, of their weight of at least one aminosilicone (AS);

16. Detergent compositions according to Claim 14, characterized in that said aminosilicone is chosen from the aminopolyorganosiloxanes comprising siloxane units of general formulae:



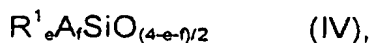
where $a+b = 3$, with $a = 0, 1, 2$ or 3 and $b = 0, 1, 2$ or 3



where $c+d = 2$, with $c = 0$ or 1 and $d = 1$ or 2



10 and optionally



where $e+f = 0$ or 1 , with $e = 0$ or 1 and $f = 0$ or 1

in which formulae,

- the R^1 symbols, which are identical or different, represent a
15 saturated or unsaturated, linear or branched, aliphatic radical containing from 1 to 10 carbon atoms or a phenyl radical, optionally substituted by fluoro or cyano groups;

- the A symbols, which are identical or different, represent a
primary, secondary, tertiary or quaternized amino group bonded to the
20 silicon via an SiC bond;

- the B symbols, which are identical or different, represent

- an OH functional group;
- an OR functional group, where R represents an alkyl group containing from 1 to 12 carbon atoms, preferably from 3 to 6
25 carbon atoms, very particularly 4 carbon atoms;
- an OCOR' functional group, where R' represents an alkyl group containing from 1 to 12 carbon atoms, preferably 1 carbon atom; or
- the A symbol.

17. Detergent compositions according to Claim 16, characterized in that

- in the units of formula (I), $a = 1, 2$ or 3 and $b = 0$ or 1 , and
- in the units of formula (II), $c = 1$ and $d = 1$.

5

18. Detergent compositions according to Claim 16, characterized in that the said A symbol is an amino group of formula:



where

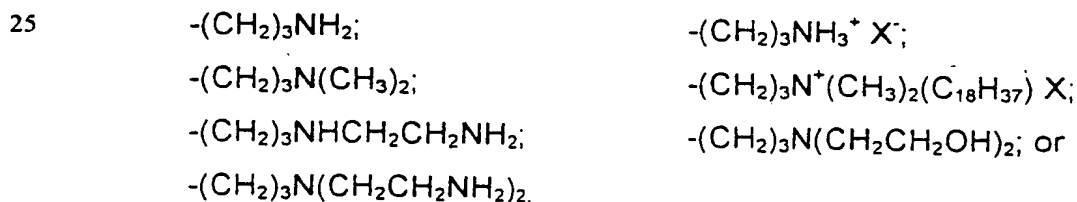
10 - the R^2 symbol represents an alkylene group containing from 2 to 6 carbon atoms, which group is optionally substituted or interrupted by one or more nitrogen or oxygen atoms,

- the R^3 and R^4 symbols, which are identical or different, represent
-H,

15 - an alkyl or hydroxyalkyl group containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, or

- an aminoalkyl group, preferably a primary aminoalkyl group, the alkyl group of which contains from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, which group is optionally substituted and/or
20 interrupted by at least one nitrogen and/or oxygen atom, said amino group optionally being quaternized.

19. Detergent compositions according to Claim 16 characterized in that the A symbol has the formula



20. Detergent compositions according to Claim 16, characterized in that the R^1 symbol represents a methyl, ethyl, vinyl, phenyl, trifluoropropyl or cyanopropyl group, very particularly the methyl group.

5 21. Detergent compositions according to Claim 16, characterized in that the B symbol represents:

- an OR group, where R contains from 1 to 6 carbon atoms, very particularly 4 carbon atoms,

- or the A symbol.

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22. Detergent compositions according to Claim 14 characterized in that said aminosilicone is at least substantially linear, preferably completely linear.

15 23. Detergent compositions according to Claim 14, characterized in that said aminosilicone exhibits a number-average molecular mass of the order of 2000 to 50,000, preferably of the order of 3000 to 30,000.

24. Detergent compositions according to Claim 14, characterized in
20 that said aminosilicone exhibits in its chain, per total of 100 silicon atoms, from 0.1 to 50, preferably from 0.3 to 10, very particularly from 0.5 to 5, aminofunctionalized silicon atoms.

25 25. Detergent compositions according to Claim 14, characterized in that said surface-active agent is anionic or non-ionic.

26. Detergent compositions according to Claim 14, characterized in that the said soluble inorganic or organic builder (B) is chosen from:

- amorphous or crystalline alkali metal silicates of formula:
30 $x\text{SiO}_2 \cdot \text{M}_2\text{O} \cdot y\text{H}_2\text{O}$, with $1 \leq x \leq 3.5$ and $0 \leq y/(x+1+y) \leq 0.5$, where M is an

alkali metal and very particularly sodium, including lamellar alkali metal silicates;

- alkaline carbonates;
- cogranules of hydrated alkali metal silicates and of alkali metal

5 carbonates;

- tetraborates or borate precursors;
- water-soluble polyphosphonates;
- water-soluble salts of carboxyl polymers or copolymers with a molecular mass of the order of 2000 to 100,000;

10 - polycarboxylate ethers;

- hydroxypolycarboxylate ethers;
- citric acid and its salts, mellitic acid, succinic acid and their salts;
- salts of polyacetic acids;

- (C₅-C₂₀ alkyl)succinic acids and their salts;

15 - polyacetal carboxylic esters;

- polyaspartic acid, polyglutamic acid and their salts;

- polyimides derived from the polycondensation of aspartic acid and/or of glutamic acid;

- polycarboxymethylated derivatives of glutamic acid; and

20 - aminophosphonates.

27. Process for protecting textiles, in particular colored textiles, by washing the said textiles using an aqueous liquor containing water and an effective amount of detergent composition comprising an aminosilicone forming the subject of Claim 14.

28. Process according to Claim 27, characterized in that the said aqueous liquor contains of the order of 0.5 to 10 grams/litre of the said detergent composition.

29. Process according to Claim 27, characterized in that the said washing is carried out at a temperature of the order of 25 to 90°C, preferably of the order of 30 to 60°C.

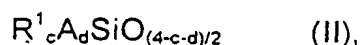
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30. A method comprising washing a colored fabric article in a washing medium comprised of a major amount by weight of water, a first minor amount by weight of a detergent and a second minor amount by weight of an aminosilicone compound chosen from the aminopolyorganosiloxanes comprising siloxane units of general formulae:

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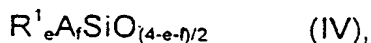


where $a+b = 3$, with $a = 0, 1, 2$ or 3 and $b = 0, 1, 2$ or 3



where $c+d = 2$, with $c = 0$ or 1 and $d = 1$ or 2

15



where $e+f = 0$ or 1 , with $e = 0$ or 1 and $f = 0$ or 1

in which formulae,

- the R^1 symbols, which are identical or different, represent a saturated or unsaturated, linear or branched, aliphatic radical containing from 1 to 10 carbon atoms or a phenyl radical, optionally substituted by fluoro or cyano groups;

- the A symbols, which are identical or different, represent a primary, secondary, tertiary or quaternized amino group bonded to the silicon via an SiC bond;

- the B symbols, which are identical or different, represent

- an OH functional group
- an OR functional group, where R represents an alkyl group containing from 1 to 12 carbon atoms, preferably from 3 to 6 carbon atoms, very particularly 4 carbon atoms

- an OCOR' functional group, where R' represents an alkyl group containing from 1 to 12 carbon atoms, preferably 1 carbon atom
- the A symbol.

5 31. A method as claimed in claim 1 wherein R⁷ is an N-(amino-alkyl)-substituted aminoalkyl group.

32. A method as claimed in claim 1 wherein R⁷ is N-(amino-ethyl)-3-aminopropyl.

10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/03366

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37 C11D17/06 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9620 Derwent Publications Ltd., London, GB; Class A26, AN 96-196723 XP002067064 "Rinse assistant for laundry detergent compsns - contains aminoalkyl-modified silicone oil(s) and inorganic silica and/or its deriv., and controls foaming in washing process" & JP 08 067 896 A (KAO CORP) see abstract</p>	14, 15
X	<p>GB 2 006 257 A (PO CORP) 2 May 1979 see claims 1-6; examples 40-7, 0-8; table 1 --- -/--</p>	14, 15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

4 June 1998

Date of mailing of the international search report

26/06/1998

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Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Int. national Application No

PCT/US 98/03366

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 713 237 A (RHONE POULENC CHIMIE) 9 June 1995 see claims; example 2 -----	14, 15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/03366

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2006257 A	02-05-1979	DE 2843709 A FR 2405991 A	26-04-1979 11-05-1979
FR 2713237 A	09-06-1995	NONE	